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Treatment of Effluent Waters from Vegetable Oil Refining

Archer Daniels Midland Co, Decatur, Ill

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A detailed investigation was done to characterize the wastewater from a vegetable oil refinery. A calcium chloride chemical treatment was installed which resulted in a net decrease in waste load of 71 percent from .0135 lb BOD_5 per pound oil processed to .0039 lb BOD_5 per pound oil processed. A further reduction of 50 percent to .0019 lb BOD_5 per pound oil processed was made by the addition of a clarifier to the treatment system. The net cost of treatment depends on the market value of the oil recovered and will range from $.032 per pound processed to a gain of $.063 per pound oil processed

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TREATMENT OF EFFLUENT WATERS FROM VEGETABLE OIL REFINING

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report, entitled "Treatment of Effluent Waters from Vegetable Oil Refining," presents the development of a chemical pretreatment method. Waste management personnel can utilize the results to reduce the BOD load up to 71%. The Industrial Pollution Control Division and the project officer can be contacted for further information on the subject.

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Director
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Cincinnati

ABSTRACT

With overloaded municipal facilities and increasingly restrictive Federal water quality regulations, it has become necessary to restrict industrial wasteloads. Vegetable oil refineries generate a high BOD_5 loading along with a high fat loading, which makes treatment difficult. Original loadings with only surface skimming as treatment generated 0.0135 kg BOD_5 per kg oil processed. After the grant period, the load was 0.0019 kg per kg processed for a reduction of 86%.

Major wastewater sources and processes are defined and described. Refinery washwater from the oil water wash centrifuges was found to be the major contributor of BOD_5 and fat, with barometric cooling tower blowdown and water from acidulation contributing smaller amounts to the load.

A calcium chloride pretreatment for the washwater which reduced the overall BOD_5 load by 71% was developed. This was done by the addition of 0.25% by weight calcium chloride to the washwater and pH adjustment to between 5 and 6. Further research was done to devise methods to further reduce the wastewater loadings to within municipal limits. Dissolved air flotation was tried without success. A consultant was retained to investigate further chemical preatment. These studies along with the recommended process for ferric chloride and lime treatment are presented.

It was felt by the grantee that the wastewater loads could be reduced to within the municipal limits by making some process modifications, increasing production supervision, and installing a clarifier to control process upsets. This program resulted in a further reduction of 50% and brought the waste strength to within municipal limits.

Cost for the system installed is $75,000 per year. Revenues from recovered by-products range from $20,000 per year to $180,000 per year, depending on the price of recovered material.

This report was submitted in fulfillment of Grant Number 12060 FDK by the Archer Daniels Midland Company, Decatur, Illinois, under the partial sponsorship of the U.S. Environmental Protection Agency. This report covers a period from March 1970 to December 1973.

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ACKNOWLEDGMENTS

This study was conducted by the Archer Daniels Midland Company, Decatur, Illinois. The initial treatment studies were conducted by James Ielase under the direction of R. S. White. In 1969, James Ielase took over direction of the study. The Roy F. Weston Company of Chicago, Illinois, was retained to investigate secondary chemical treatment and to design a ferric chloride and lime treatment system. Arnold Johnson, refinery project engineer, supervised construction of the clarifier and treatment system. Donald Gill developed the operation procedures and process modifications after the system was installed and prepared the final report. James Curry assisted with the analytical work throughout the grant period.

This report was submitted in fulfillment of Grant No. 12060 FDK. Clifford Risley, Jr. was the project officer during the grant. David Rickles was the assistant project officer during the research and construction phase. Ronald Eng was the assistant project officer during the preparation of the final report. He and James Scaief, research representative, Corvallis, Oregon, provided assistance in the final report preparation. Special recognition is made of the efforts of Jack L. Witherow of the Food and Wood Products Branch, Corvallis Field Station, IERL-Cincinnati. Mr. George Rey, EPA staff engineer, Washington Headquarters, provided technical assistance in the early stages of the project.

SECTION I

INTRODUCTION

The Archer Daniels Midland Co., Inc., processes oilseeds, primarily soybeans. Oil is solvent-extracted from the seeds and refined at three locations--two at Decatur, Illinois, and one at Lincoln, Nebraska. The refining of vegetable oils generates several wastewater streams that have caused the plants to exceed acceptable waste strength limits set by their respective municipal authorities. The object of this project was to analyze these waste streams and devise treatment methods by which their BOD_5 and fat strength could be reduced to acceptable levels.

The initial problem was to identify the waste streams and to characterize the wastewater. The second problem was to determine optimum treatment for each source and finally to implement the necessary equipment and procedures.

The initial investigation and design was done by ADM in conjunction with a consulting firm. These investigations are described in Sections V, VI, and VII.

Because of significant process modifications described in Section VIII, it was determined that some of the process recommendations would not be necessary. Provisions were made for their future installation if they proved to be necessary.

A description of equipment installed and results obtained are contained in Section VIII.

SECTION II

CONCLUSIONS

The wastewater survey done after the calcium chloride system was installed determined that for a soybean processing facility, the refinery produces approximately 90% of the wasteload and the extraction plant contributes only about 10%. Of the refinery wastewaters, the washwater is the largest source of BOD_5 and fat. For a facility processing 385,500 kg (850,000 lb) per day of oil, this stream contributes 450 to 22,700 kg (1000 to 50,000 lb) per day of BOD_5 and fat in the form of water soluble soaps. Greasy cooling water can contribute 340 kg (750 lb) of fat and BOD_5. Acid water contributes approximately 30 kg (70 lb) of fat and 1800 kg (4000 lb) of BOD_5 per day. Floor washings and car washings can contribute significant and highly variable loadings. Any of these sources can contribute many times the normal loading under conditions where the process is upset or uncontrolled.

Treatment of the washwater with 0.25% by weight calcium chloride resulted in an overall reduction of 71% of the BOD_5, from 0.0135 to 0.0039 kg BOD_5 per kg oil processed. Process modifications, increased process control, and a clarifier resulted in a further reduction in total load of 50% of both the fat and COD. A greater reduction would have been obtained had the plant not started to refine corn oil at approximately the same time the clarifier was started. Installation of the clarifier in Lincoln, where corn oil is not refined, resulted in a reduction of 65% of the COD and fat. The overall reduction in Decatur for both the calcium chloride and clarifier was 86%, from 0.0135 kg BOD_5 per kg oil processed to 0.0019 kg BOD_5 per kg oil processed.

Laboratory studies indicated that secondary chemical treatment with ferric chloride and lime would result in a reduction of 85% of the fat and 65% of the COD over the calcium chloride treatment. This would be an overall reduction of 95% of the fat and 90% of the COD.

The calcium chloride treatment system was installed in 1970 at a cost of $25,000. Treatment cost based on 10 years straight line depreciation is $32,308 per year. The system removes approximately 1206 kg (2660 lb) per day fat and 3736 kg (8236 lb) per day BOD_5. This is a cost of 2.34¢ per kg (1.06¢ per lb) BOD_5 and 7.28¢ per kg (3.3¢ per lb) fat removed.

The clarifier was installed in 1971 at a cost of $96,000. Annual depreciation cost, based on 5.5% per year, is $5,367. Total treatment cost for the clarifier is $42,961 per year. The system removes approxi-

mately 778 kg (1716 lb) per day BOD_5 and 190 kg (420 lb) per day fat. This is a cost of 61.95¢ per kg (28.1¢ per lb) fat and 15.15¢ per kg (6.87¢ per lb) BOD_5 removed.

The net cost for the treatment system is 14.77¢ per kg (6.7¢ per lb) fat removed, 4.56¢ per kg (2.07¢ per lb) BOD_5 removed, and 36¢ per 1000 liter ($1.36 per 1000 gal) water treated. This cost is offset by revenue from recovered oil that can be sold. The price of this oil has varied over the grant period from 8.8¢ to 39.7¢ per kg (4¢ to 18¢ per lb). This results in a net treatment cost that has varied from 25¢ per 1000 liter (95¢ per 1000 gal) to a gain of 51¢ per 1000 liter ($1.93 per 1000 gal). On a basis of oil processed, this is .032¢ per kg (.015¢ per lb) oil processed to a gain of .063¢ per kg (.028¢ per lb) oil processed.

Installation of the ferric chloride and lime treatment system is estimated to cost $100,300 per year compared to $43,000 for the system installed. The estimated fat recovered would be approximately 324 kg (714 lb) per day at a cost of $275 per day, or 84.9¢ per kg (38.5¢ per lb) fat, which is 37% higher than the installed treatment.

SECTION III

RECOMMENDATIONS

Further research should be done to develop uses for and modifications of corn lecithin to reduce the wasteload from refining corn oil.

Additional study is also needed to determine the effect the ferric chloride and lime treatment system would have on the reduced waste load compared to the load at the time the secondary chemical treatment was done.

A further major reduction in BOD_5 would result in the development of a good treatment system for the acid liquor. This was not an important consideration during this grant period because after the development of the calcium chloride treatment for wash water, the plant was well within the BOD_5 limit specified by the municipality.

SECTION IV

PROCESS DESCRIPTION

This section describes a soybean extraction plant and refinery common to Decatur and Lincoln. Additional corn germ extraction and refining in Decatur is entirely analagous to the soybean process and will not be described separately. Only those processes that generate significant waste products will be described in detail. All processes operate 24 hours per day and 7 days per week. The plant in Decatur has the capacity for 120,000 bushels per day soybean extraction, and 200 tons per day of corn germ, and the capacity to refine 1.4 million lb per day of vegetable oil. Figures 1 and 2 describe extraction and oil refining respectively.

SOYBEAN PREPARATION AND EXTRACTION

The beans are initially cleaned by mechanical screening. They are then cracked and cleaned by aspiration. This is followed by heat conditioning in a steam tube drier. The cracks are flaked by flaking rolls and conveyed to an extractor. The oil is removed by continuous countercurrent hexane extraction. The flakes are then conveyed to the desolventizer toaster where the volatile solvent is driven off by jacket and sparge steam. The vapors are condensed and the liquor pumped to a gravity separator. The water insoluble hexane is sent to solvent storage and the water discharged to the sewer. The desolventized and toaster flakes are cooled, blended and loaded. The oil-hexane mixture is pumped to distillation where the solvent is evaporated off and condensed. The oil is then pumped to storage. The condensate water from this process contains some entrained oil and soluble protein but is not a major source of BOD_5 or fat (See Section V).

SOYBEAN OIL REFINING

The refining of vegetable oil may employ a combination of several processes, depending on the product desired. These processes include degumming, caustic refining, subsequent washing, vacuum drying, bleaching, hardening, post bleaching, filtration and deodorization.

Degumming

Approximately 2% water is added to the oil to hydrate the gums (phosphatides). On hydration these gums become oil insoluble and are separated from the oil in a centrifuge. The gums are then dried to produce lecithin.

This step can be bypassed; however, it decreases the amount of soapstock produced in caustic refining and in the case of soybean oil, produces a valuable by-product.

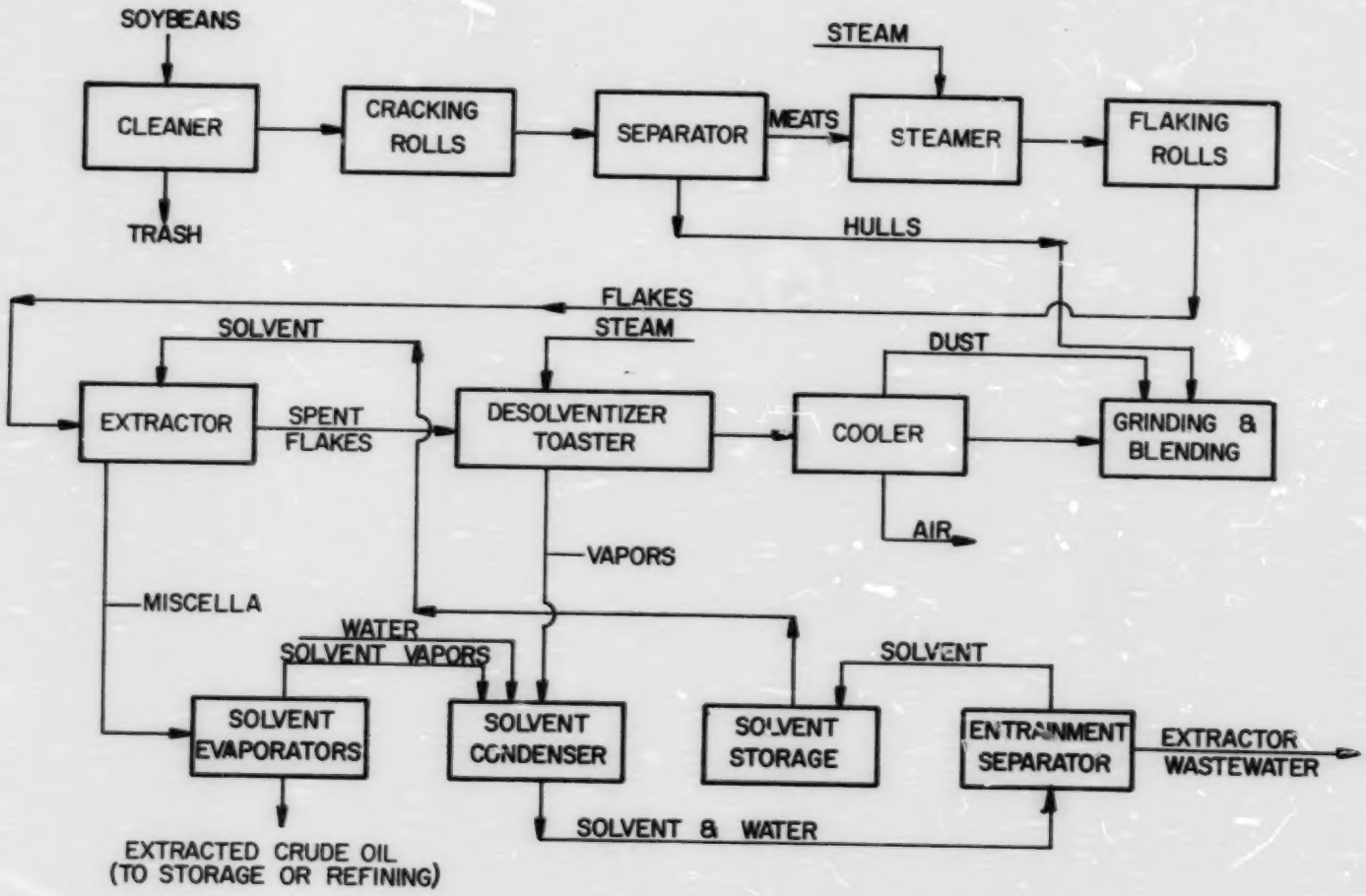


Figure 1. Soybean preparation and oil extraction flow diagram (typical Lincoln and Decatur).

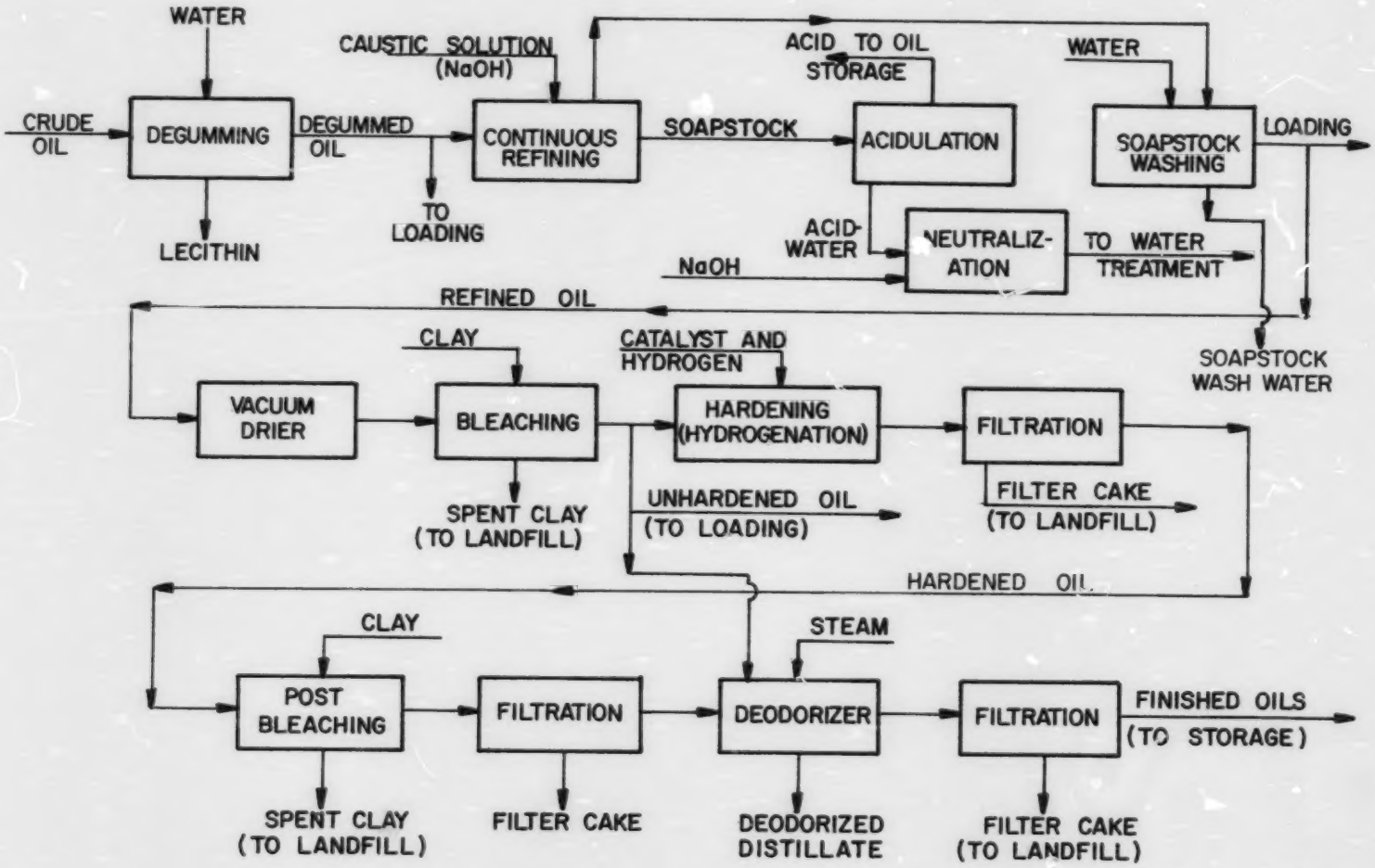
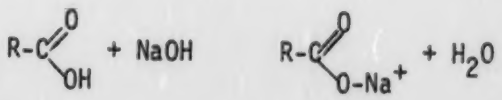


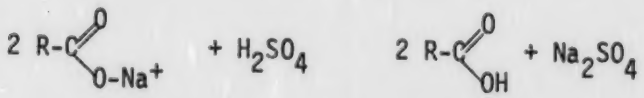
Figure 2. Oil refining flow diagram.

Caustic Refining

Soybean oil is primarily triglyceride with approximately 0.5% to 1.0% free fatty acids. The object of caustic refining is to convert the free fatty acids to water soluble soaps and then to remove them by centrifugation. A 12% sodium hydroxide water solution is mixed with the oil. The water soap solution and oil is then separated in a centrifuge. The chemical equation for this reaction is:



The water soap solution (called soapstock) is pumped to acidulation where sulfuric acid is added on a batch basis to convert the soaps to fatty acids. The fatty acids are insoluble in water and float to the surface. The mineral salts and any water soluble material remains in the water layer. The water layer is neutralized and discharged to the waste treatment facilities. The chemical equation for this reaction is:



Water Wash

The oil from caustic refining contains trace amounts of soaps and sodium hydroxide. Condensate water is added to the oil and agitated to remove this residual material. The oil and water from this process is a weak (1% to 3%) soap solution with a relatively high pH.

Vacuum Drying

The oil from water washing contains trace amounts of water that can blind the filters in subsequent filtration operations. In vacuum drying the oil is heated under a vacuum of 28" Hg to remove this trace moisture. There is no significant waste stream from this process.

Bleaching

Trace amounts of color bodies are removed by absorption onto activated bleaching clay. The clay and oil are slurried and heated under vacuum. The clay is then removed in pressure filters and disposed of in the municipal landfill.

Hardening

Hardening is employed to raise the melting point of the oil for use in shortening or margarine manufacture. This is done by the addition of hydrogen to unsaturated oil molecules over a nickel catalyst. The catalyst is

blended with the oil and heated. The hydrogen gas is then bubbled through the mixture. The degree of hardening is determined by the temperature, pressure and quantity of hydrogen gas added to the reaction. The catalyst is filtered out of the oil after the reaction is complete. No significant wastewater is generated by hydrogenation.

Deodorization

The purpose of deodorization is to remove volatile impurities that might cause flavors and odors. This is done by steam distillation at temperatures of 425°F to 475°F and 3 mm Hg absolute pressure. The high temperatures are obtained with a dowtherm boiler heating system. The vapors are pulled off through the vacuum system. (See Figure 3) A recycle deodorizer distillate scrubber removes the bulk of the organic material from the vapor (99%+). Excess distillate is pumped to storage and sold as a valuable by-product. Deodorizer distillate is a valuable source of α-tocopherol (Vitamin E). The remaining vapors, primarily steam, are condensed in the water scrubber along with any remaining organic material and drain to the greasy cooling tower hot well.

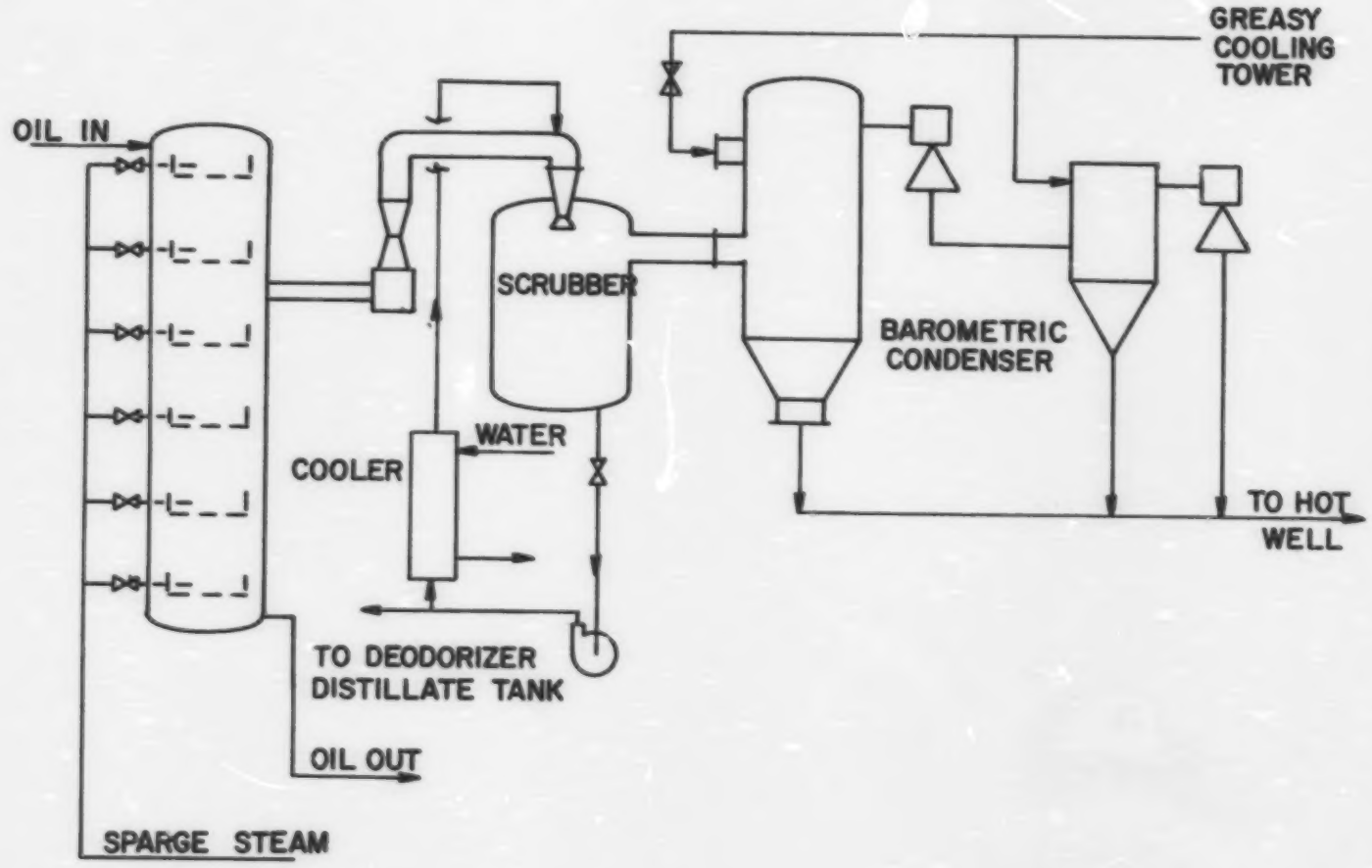


Figure 3. Deodorization flow diagram.

SECTION V

WASTEWATER SOURCES, ANALYSIS, AND QUANTITIES

All analyses except COD were conducted according to the test procedures given in Standard Methods for Analysis of Water and Wastewater, 12th Edition. The test procedure for COD is given in Appendix C. This modified procedure was used because of the shorter reflux time and because it is more closely related to BOD5 than the standard method. This modified COD will be denoted by quotation marks. Figure 4 compares the COD analysis to the BOD_5 analysis.

Flows and wastewater analysis for each wastewater source are presented in Figure 5.

The condensate water is generated in heating coils and jacket steam throughout the refinery. It is generally hot, clean water and most of it is being recycled as washwater in the refining step.

Washwater generated in the oil washing step is high in BOD and fat primarily because of dissolved soaps. The stream will contribute 1000 to 5000 lb per day of fat or BOD_5 to the sewer load. If the oil is not degummed before caustic refining, some water soluble phosphatides will be removed in this step and will cause higher loads. This is generally the case when corn oil is being processed.

Floor washings are highly variable for obvious reasons. It is characterized by high temperature and high pH because of the washing equipment and soaps.

Greasy cooling water can be a major source of BOD_5 depending on the operation of the deodorizer scrubber and atmospheric conditions. (See deodorization description Section IV) Any organic material that passes through the scrubber becomes emulsified in the greasy water in the vacuum system. The greasy cooling tower dissipates the heat of condensation of the steam primarily by evaporation of the greasy water. In cold weather the water loses more heat by convection which decreases the amount of evaporation necessary. When the amount of water entering the tower via steam condensation is greater than the wind drift plus evaporation, it becomes necessary to blow down the tower to the sewer. The organic material in the water is primarily short chain free fatty acids. Typical COD values range up to 3000 mg per liter. For an overflow of 30,000 gal per day, 750 lb of COD would be discharged to the sewer based on 3000 mg per liter of fat.

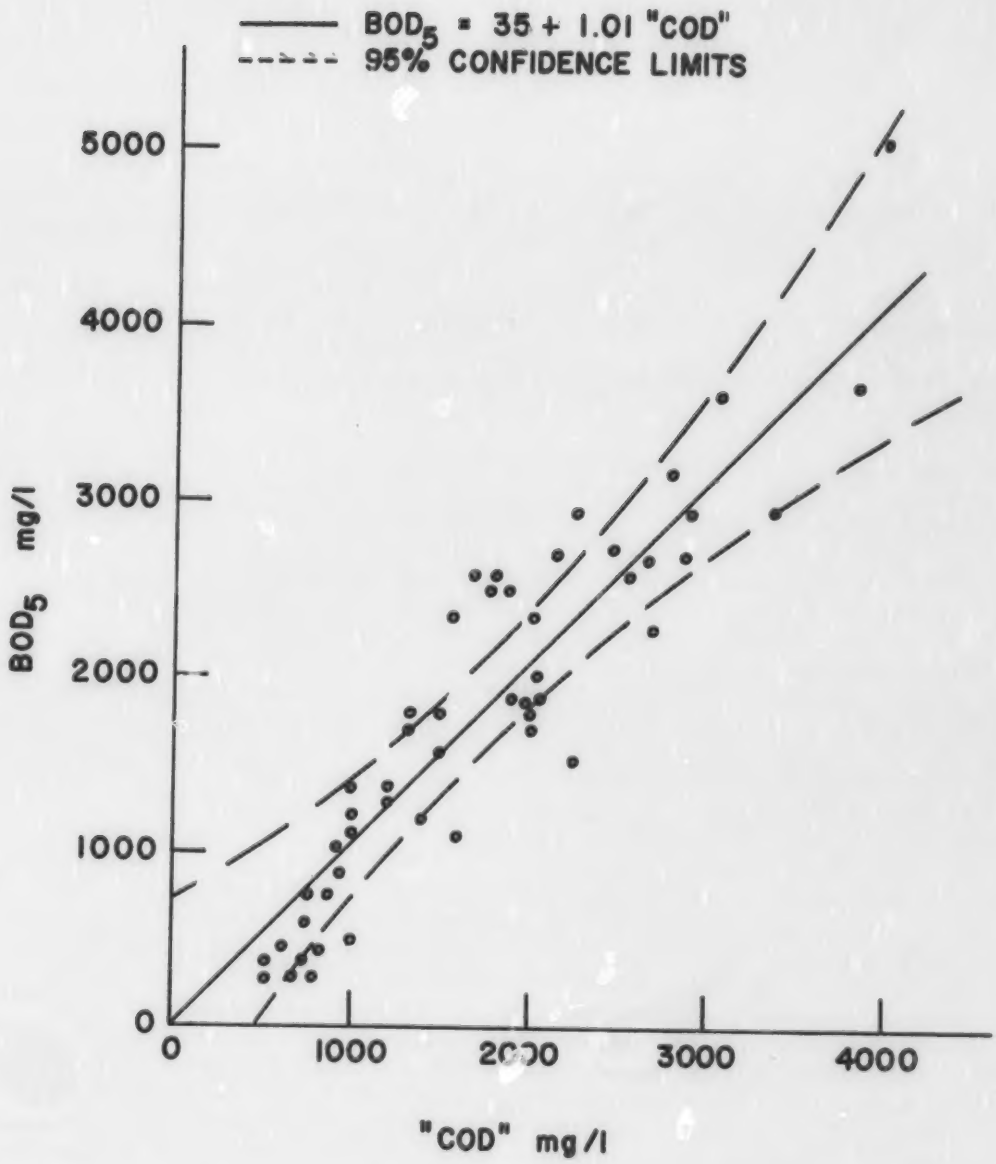


Figure 4. BOD and COD correlation for total West plant effluent.

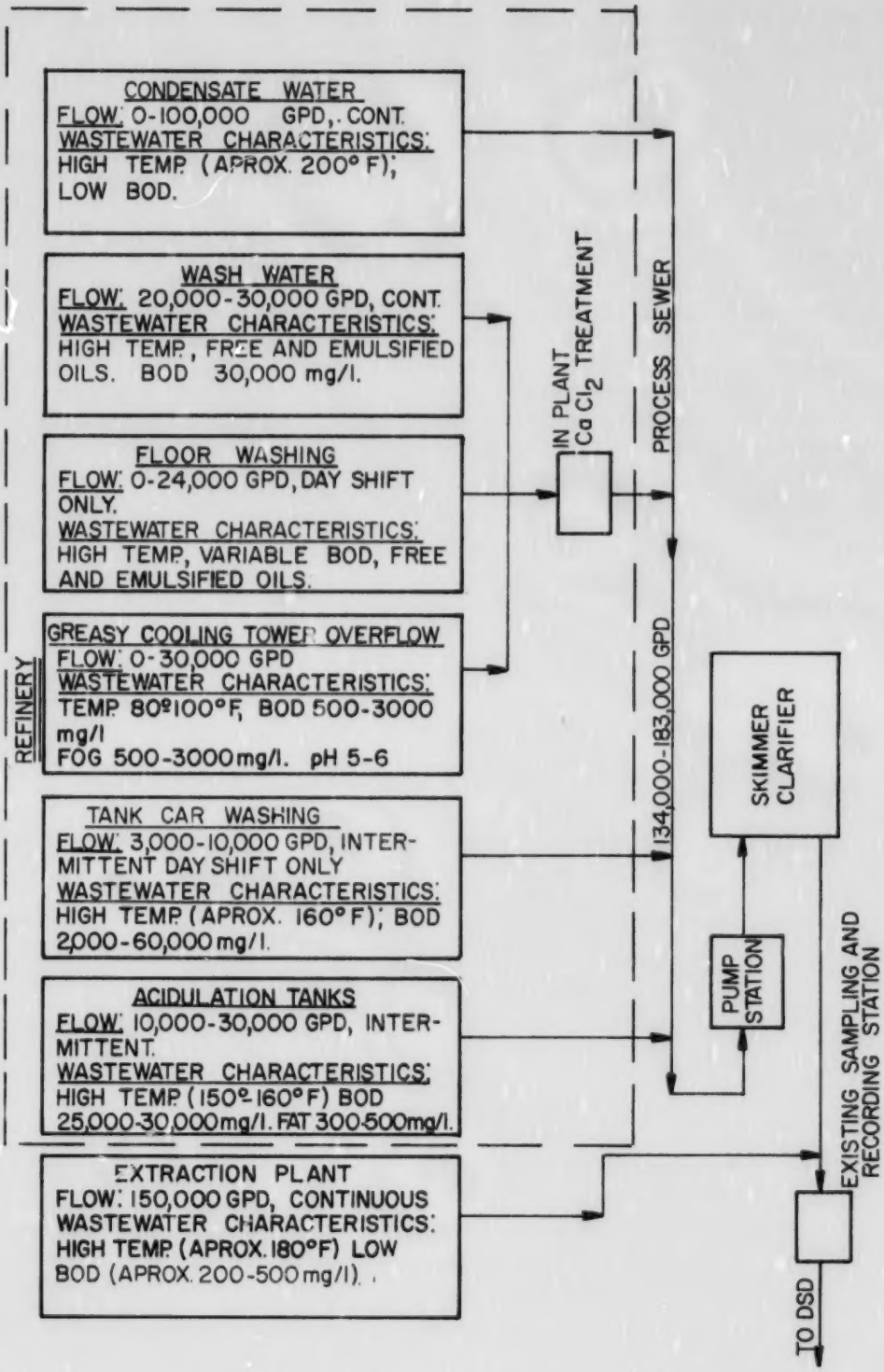


Figure 5. Schematic of major wastewater sources.

Tank car washings vary from one to four cars per day. The effluent is characterized by high temperature, 160°F, and a variable amount of emulsified oil. The BOD_5 can be anywhere from 2000 to 60,000 mg per liter. (Table 1)

The neutralized acidulation water flow and COD is highly variable depending upon the amount of flush water being used on the centrifuges and whether or not the oil is being degummed prior to the refining. The phosphatides which would be removed in degumming greatly increase the strength of the acidulation water due to their water solubility. Fresh water can increase the moisture content of the soap from 50% to 95%. While this does not affect the total BOD_5 load, it does reduce the residence time in treatment facilities and reduces the processing time which is necessary to get good oil separation. While the BOD_5 is very high (25,000 mg per liter) for this stream, the fat is relatively low (300 - 500 mg per liter). This is the only waste stream from the refinery that is not composed primarily of hexane soluble material. A typical day would yield loadings of 4000 lb per day BOD and 70 lb of fat based on 20,000 gal at a 25,000 mg per liter BOD_5 and 400 mg per liter fat.

The extraction plant wastewater consists of condensate described in the process section. At 150,000 gal per day and 300 mg per liter BOD, this stream contributes only 375 lb per day of BOD. The temperature is high (180°F) and the pH is near neutral (6 - 8). Flows were estimated from process design requirements. (Table 2)

TABLE 1. CHARACTERISTICS OF REFINERY WASTEWATER COMPONENT STREAMS GRAB SAMPLES

Source	Sampling Date	Sampling Time	Wastewater Characteristics COD (mg/l)	pH	Temp. (°F)
Acidulation Tank	9-09-69	4 p.m.	26650	5.6	1150-160
Acidulation Tank	9-11-69	--	29220	4.6	150-160
Acidulation Tank (Settled Sample)	9-11-69	9:30 a.m.	24760	5.0	150-160
Tank Car Washing (Crude Oil)	9-11-69	2 - 6 p.m. (Composite)	60400	6.0	150-160
Tank Car Washing (Hydrogenated)	9-11-69	(Composite)	4655	6.1	150-160

TABLE 1. CHARACTERISTICS OF REFINERY WASTEWATER COMPONENT STREAMS GRAB SAMPLES (Continued)

Source	Sampling Date	Sampling Time	Wastewater Characteristics COD (mg/l)	pH	Temp. (°F)
Tank Car Washing (Hydrogenated)	9-16-69	(Composite)	2100	6.7	150-160

TABLE 2. EXTRACTION PLANT LOADING

Sample Date	BOD_5 (mg/l)	Estimated Flow (GPD)
Extraction Plant		
9-24-69	325	150,000
9-26-69	496	150,000
9-30-69	370	150,000
10-01-69	360	150,000
10-02-69	370	150,000
Average	384	150,000

SECTION VI

PRIMARY CHEMICAL TREATMENT

The initial objective was to determine by laboratory experimentation whether a chemical pretreatment of any waste water stream was feasible. Several chemicals, including polymers, polyelectrolytes, sodium chloride and calcium chloride were used. Calcium chloride was found to be the most economical and efficient coagulant at dosages of approximately 0.25% by weight. The equation for this reaction is:

$$2\ R\text{-}C(=O)\text{-}O\text{-}Na^{+} + Ca^{++} \qquad 2\ Na^{+} + (R\text{-}C(=O)\text{-}O^{-2})\ Ca^{++}$$

The normal pH of the washwater was in the range of 10.5 to 12.5 and while some separation was accomplished at this pH, a more rapid and effective coagulation and separation occurred at a lower pH. After the addition of the calcium chloride to the washwater, an adjustment to the 5 - 6 pH range with sulfuric acid greatly enhanced the speed of flotation and made the floc more dense. Table 3 shows COD reductions using this chemical treatment on the washwater. The average reduction in COD was 91.7%.

TABLE 3. LABORATORY WASHWATER COD REDUCTION BY CALCIUM CHLORIDE TREATMENT* AND pH ADJUSTMENT

Test	COD Before Treatment (mg/l)	COD After Treatment (mg/l)
1	25142	2280
2	26560	3750
3	39000	3176
4	51000	3276
5	29366	2061
6	44662	4008
7	17766	934
Average	33356	2783

*Calcium chloride added was 0.25%.
+Average reduction was 91.7%.

Because of the success of the laboratory investigations, primary treatment units were installed at all ADM refineries. Figure 6 shows the plant layout used for this system. The washwater from the water wash centrifuges is discharged into the 5500 gal tank on a continuous basis. Calcium chloride is added by a chemical feed pump and a roto-meter was installed to insure proper proportioning. The residence time in the 5500 gal tank is dependent upon the rate of refining and the amount of floor washings being discharged to the system. Because of this, some of the floc is usually recovered in sedimentation tanks later in the system. Acid is added to the second tank to increase the density of the floc and to increase the rate of the rising flocculated soaps and oils. The effluent from this tank is pumped to an oil skimmer located outside the refinery. The recovered soaps and oils are pumped to soapstock storage and acidulated.

Table 4 shows the average Decatur East BOD_5 figures for water discharged to the municipal sewer for May 1968 before the calcium chloride treatment was installed and May 1970 after the calcium chloride treatment was installed. No acidulation is done at Decatur East so the 93.3% overall reduction is indicative that the process is as effective as expected from laboratory studies on washwater only. Overall BOD_5 was reduced at the West Plant by 71%, the difference being due to acidulation. (See Table 14, Section VIII)

Part of the original grant agreement was to investigate a washwater recycle process with financing from the United States Department of Agriculture. The washwater would have been recycled through an ion-exchange unit to convert the soaps to free fatty acids. The grantee submitted a proposal for $45,000 for a pilot unit which was rejected. Development of the calcium chloride treatment had minimized the importance of the ion-exchange process so the project was droppec

TABLE 4. WASTEWATER BOD_5 BEFORE AND AFTER $CaCl_2$ TREATMENT INSTALLATION:* EAST PLANT DISCHARGE TO MUNICIPAL SEWER

Test	BOD_5, May 1968, Before $CaCl_2$ (mg/l)	BOD_5, May 1970, After $CaCl_2$ (mg/l)
1	1340	335
2	1620	70
3	1270	30
4	1730	170
5	2710	380
6	2650	100
7	2720	245
8	2350	125
9	1595	70
10	2250	50

TABLE 4. WASTEWATER BOD_5 BEFORE AND AFTER $CaCl_2$ TREATMENT INSTALLATION:* EAST PLANT DISCHARGE TO MUNICIPAL SEWER (Continued)

Test	BOD_5, May 1968, Before $CaCl_2$ (mg/l)	BOD_5, May 1970, After $CaCl_2$ (mg/l)
11	2055	155
12	2710	680
13	5200	545
14	3620	85
15	2100	155
16	2100	90
17	2100	80
18	2100	100
19	2100	25
20	2100	55
21	2100	25
22	2100	100
23	2100	85
24	2070	105
25	1900	55
26	2100	40
27	3610	25
28	3300	85
29	2590	90
30	2360	50
31	2460	620
Average	2358	156

*Reduction in BOD_5 was 93.3%.

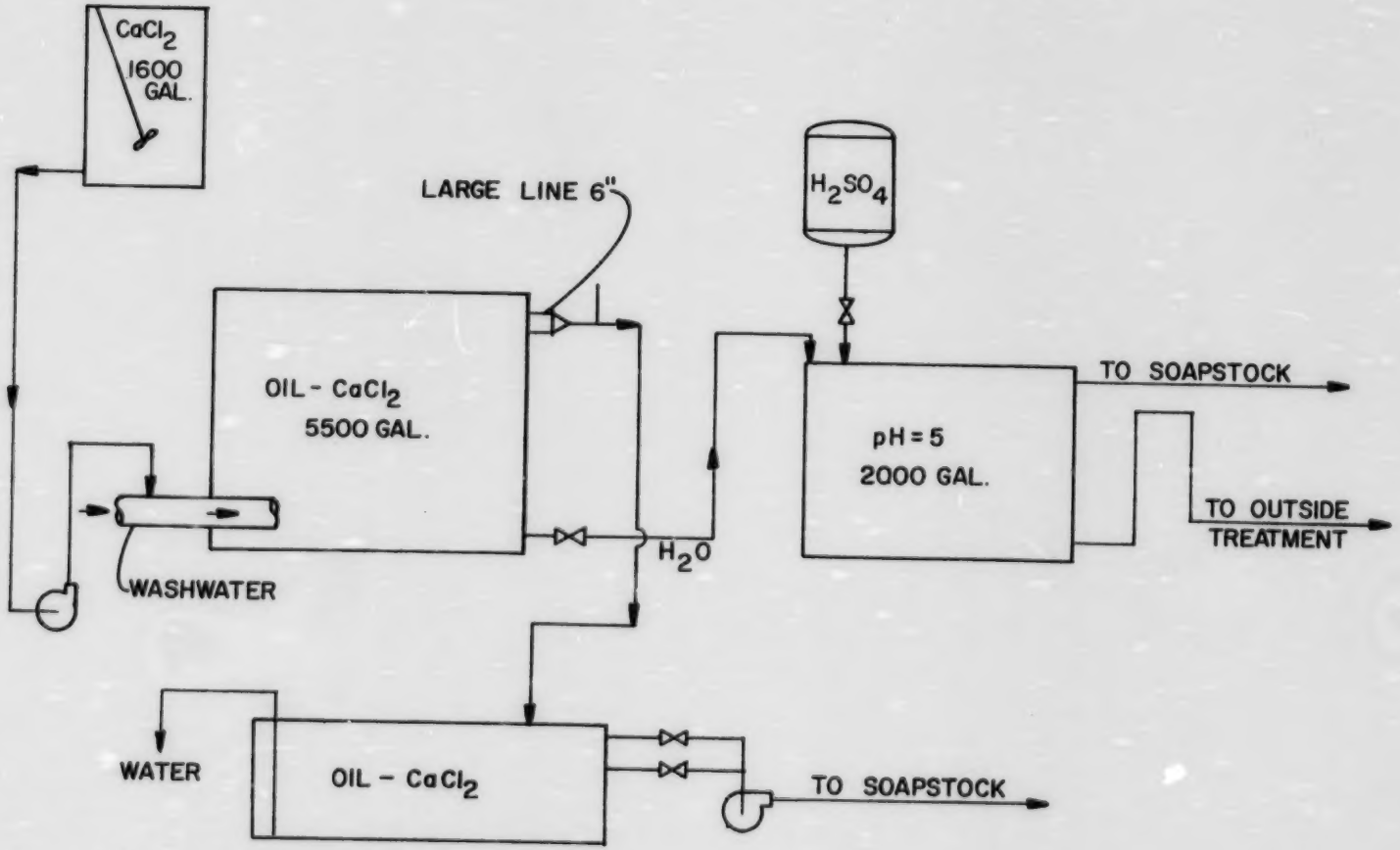


Figure 6. $CaCl_2$ water treatment flow sheet.

SECTION VII

TREATABILITY STUDIES AND DESIGN BASIS

While chemical treatment of the washwater from the refineries resulted in an overall reduction in the total waste stream from approximately 50,000 P.E. to 20,000 P.E., there was still a problem resulting from other wastewaters in the refinery complex which did not respond as readily to the calcium chloride treatment. Further studies were needed to reduce the organic load to within acceptable limits.

A consulting firm was retained to assist in the investigation of secondary chemical treatment and to design a treatment process based on these investigations. At the same time, the grantee was to investigate the possibility of treatment with air flotation and process modifications to reduce the waste load.

GAS FLOTATION STUDIES

Laboratory studies indicated that finely dispersed gas bubbles produced by electrolysis will rapidly remove most suspended solids from a waste stream and materially reduce the BOD.

Two grids consisting of an anode and cathode were immersed in the bottom of a chamber and low voltage current was passed between them. Electrical current was supplied to the grids with a 20 ampere rectifier. A direct current of approximately 2-5 volts and 4-8 amperes was introduced to the grids which were one half square foot in area. Hydrogen was generated at one grid and oxygen at the other in the form of very fine bubbles evenly distributed over the area. As the bubbles rose, they attached themselves to the suspended solids and entrained oils and floated them to the top.

With this procedure, settleable solids as well as suspended solids were floated to the surface. Satisfactory results were usually obtained within fifteen minutes. (Table 5) The data obtained from these experiments showed a reduction of organic loading of approximately 50%, from 7021 to 3231 mg per liter, beyond the results obtained with the primary treatment which consists of the already outlined calcium chloride system.

TABLE 5. LABORATORY COD REDUCTION WITH GAS FLOTATION

Material	Test	Before COD (mg/l)	After COD (mg/l)
Greasy Water	1	3005	248
Washwater	1	29,019	777
Skimmer Effluent	1	1,606	331
	2	2,565	1,250
	3	2,850	1,650
Water to Sanitary District	1	1,140	331
	2	1,238	228

An electrolysis unit was then installed in the refinery skimmer. One hundred sixty square feet of 1/2 inch steel floor grate was used for the anode and cathode. The grids were placed in the bottom of the skimmer on bricks approximately 3 inches apart. Power was supplied by a 1500 ampere Clinton rectifier model number R1512HO-S. Results seemed to be promising; however, after a few weeks of operation, the production of gas bubbles all but stopped. Upon emplying the skimmer and inspecting the grids, the cathode was in excellent condition and showed no corrosion; however, the anode was almost completely eroded.

Laboratory studies were resumed, and it was found that on prolonged usage, the anode was indeed eroded while the cathode remained in good condition. Studies were then undertaken to find a suitable anode material to withstand this eroding effect.

Anodes of iron, aluminum, titanium, 316 stainless steel, Inconel, cast iron, monel, nickel and high silica iron were tried without success. A combination of 316 stainless steel mesh with graphite supports for the anode gave the best laboratory results.

A plant scale installation was made with grids consisting of 18 mesh stainless steel with graphite cross bars. After a period of two weeks, the skimmer was drained and the grids inspected. The anode consisting of stainless steal and graphite was badly deteriorated. The stainless steel mesh was almost completely gone and the graphite had decreased in size considerably. The efficiency had deteriorated over the two week period to a point where few bubbles were observed coming to the surface of the water. During the first few days of operation, the process worked very well producing a diffuse bubble blanket.

Another consultant was then employed to develop a workable anode. This firm produces material used specifically for this application and they felt their material would stand up under the conditions of the process. The material consisted of graphite bars 48 inches long, 6 inches wide and 1 inch thick coated with lead dioxide. Eight bars were purchased and installed in the Imhoff tank. Copper buss bars coated with glyptol, an insulating material, to prevent corrosion were used to connect the graphite bars. The coating did not withstand the corrosion and in two days was almost completely destroyed.

Graphite connecting bars were then tried and proved to be more successful. After 1 week of operation, the graphite anodes were badly eroded and began breaking under their own weight.

Advances made in other methods of waste control had minimized the importance of the development of this system. At this point, the electrolysis system was abandoned as being impractical.

SECONDARY CHEMICAL TREATMENT

Studies were undertaken by the consultant in September 1969 to do the following:

1. Establish the flows and characteristics of the West Plant Refinery, Extraction and Subsurface drainage streams.

2. Do chemical/physical treatability studies on the refinery skimmer effluent.

3. Develop process design parameters from the above treatability studies.

4. Propose a treatment facility capable of treating these wastewaters.

The treatment requirements were set by the Decatur Sanitary District and consist of the following:

a) For 95% of the time the total Biochemical Oxygen Demand of waste from all industry facilities, in the aggregate, shall not exceed 5780 lb per day (34,000 P.E.) as any 10-day average nor exceed 7,200 lb per day (42,500 P.E.) as any 3-day average.

b) The total fats-oils-grease of the waste from the three plants shall not exceed 1000 lb per day as a monthly average, shall not exceed 1,00 lb per day for more than 10% of the samples, and shall be less than 2,000 lb per day for 97% of the samples. The sanitary district reserves the right to re-examine these criteria if, after they are met, physical and treatment problems resulting from the grease content of the waste continue.

Figure 7 is a location plan of the sampling points used in the study. Grab samples, representative of skimmer effluent, were collected at the lagoon inlet (sampling point No. 1) at 2-hour intervals over a period of 3 days from September 9 to September 12, 1969.

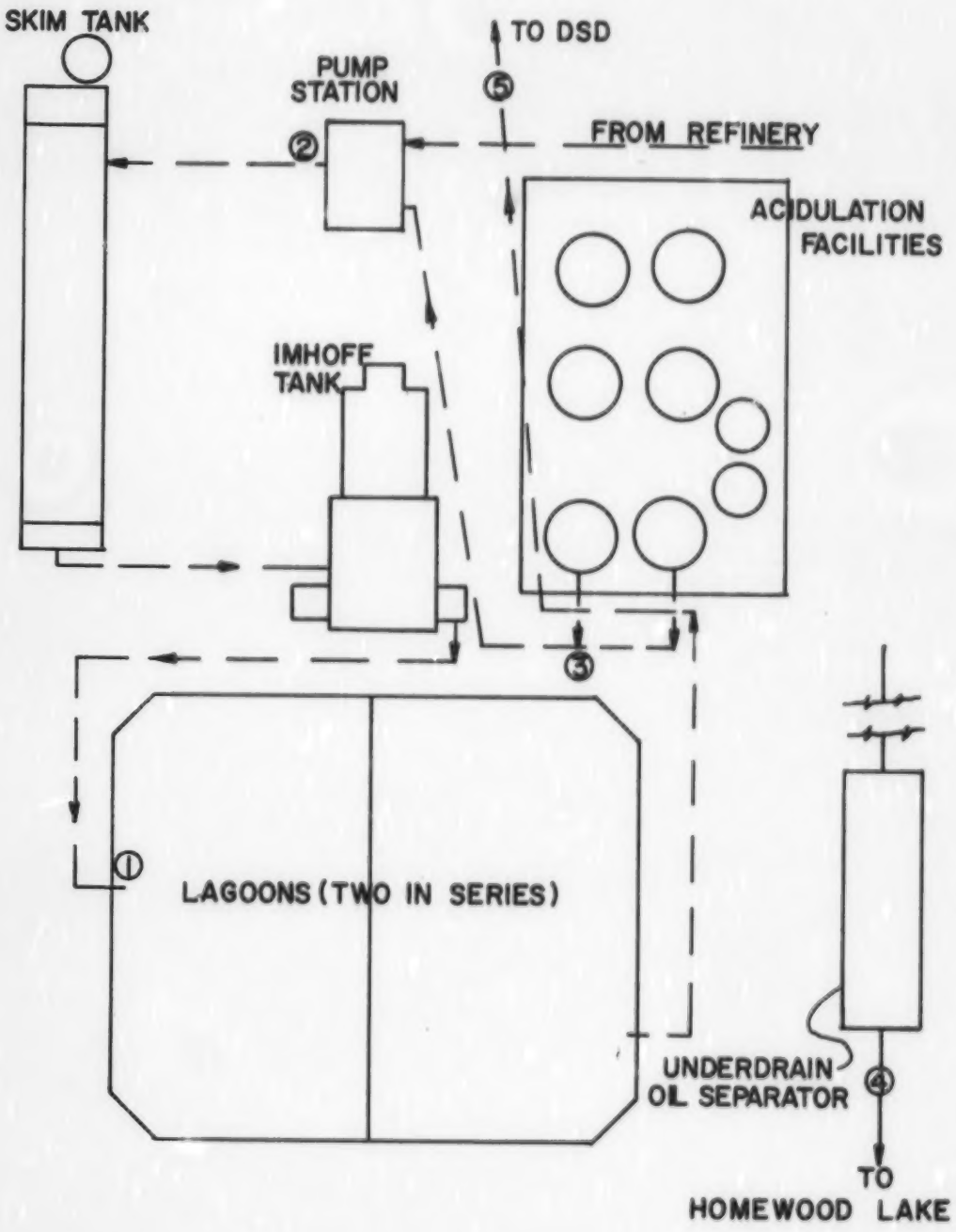


Figure 7. Treatment flow diagram during water survey.

TABLE 6. CHEMICAL FLOCCULATION SCREENING TEST RESULTS FOR WEST REFINERY SKIMMER EFFLUENT

Raw Sample									
Collection Date and Time	Type of Sample	Characteristics COD mg/l	PH	Temp °F	Treatment Coagulants Type	Coagulants Dosage, mg/l	Coagulant Aid Type	Coagulant Aid Dosage, mg/l	Qualitative Observations and Conclusions from Jar Test Results
9-9-69 11:30 a.m.	Grab	6,400	6.2	155	$FeCl_3$	100 to 1000	--	--	$FeCl_3$ dosages below 1000 mg/l did not seem to have any significant effect on breaking the emulsion. The supernatent with $FeCl_3$ dosages at less than 1000 mg/l after centrifugation still was very turbid. 1000 mg/l dosage gave food flocs and relatively clear supernatent. The $FeCl_3$ treatment at a dosage of 1000 mg/l was judged as effective.
--	--	--	--	--	$Ca(OH)_2$	200 to 1000	--	--	Floc formation was poor at 200 mg/l dosage. Supernatent was turbid after centrifugation. However, 400 mg/l to 1000 mg/l dosage gave good flocs and clear supernatent after centrifugation floc formation was almost instantaneous. The pH at these dosages valued from 7 to 8. The $Ca(OH)_2$ treatment above 400 mg/l was judged as effective.
--	--	--	--	--	$CaCl_2$	200 to 2000	--	--	There was no apparent flocculation. No change in clarity after centrifugation, no sludge formed at the bottom. $CaCl_2$ treatment at all dosages was judged as ineffective.
--	--	--	--	--	$Fe_2(SO_4)_3$	100 to 1000	--	--	No flocculation was observed up to 5000 mg/l dosage. Supernatent was very turbid with very slight sludge at the bottom after centrifugation. pH was 5.9 at 100 mg/l dosage and 5.4 at 500 mg/l dosage. 1000 mg/l dosage gave good flocculation with clear supernatent after centrifugation. pH was 5.0 $Fe_2(SO_4)_3$ treatment at a dosage of 1000 mg/l was judged as effective.

TABLE 6. CHEMICAL FLOCCULATION SCREENING TEST RESULTS FOR WEST REFINERY SKIMMER EFFLUENT (Continued)

Raw Sample					Treatment				
Collection Date and Time	Type of Sample	Characteristics COD mg/l	pH	Temp °F	Coagulants Type	Coagulants Dosage, mg/l	Coagulant Aid Type	Coagulant Aid Dosage, mg/l	Qualitative Observations and Conclusions from Jar Test Results
--	--	--	--	--	$Al_2(SO_4)_3$	100 to 1000	--	--	Flocculation was very poor up to 500 mg/l dosage. At higher dosage there was some improvement in supernatent clarity. However, the results were still poor. The pH was 5.8 at 100 mg/l and 5.3 at 1000 mg/l dosage. $Al_2(SO_4)_3$ treatment was judged as ineffective.
9-9-69 3:30 p.m.	Grab	19,000	7.5	148	$FeCl_3$	200 to 1500	--	--	At 200 mg/l dosage there was no noticeable effect. At 300 mg/l dosage the flocs formed after 10 mins. Some floated at the top, some settled down. The sample was still very turbid. Centrifugation did not improve the clarity. 500 to 1500 mg/l dosage gave large amount of flocs through out the depth. Centrifugation gave some sludge at bottom, some scum at the top and still large amounts of flocs throughout the depth, indicating that the mass density of the flocs was same as that of the wastewater. pH at a dosage of 500 mg/l was 6.6 and that at 1500 mg/l was 40. The $FeCl_3$ treatment on this sample was judged as ineffective.
--	--	--	--	--	$Ca(OH)_2$	100 to 2000	--	--	Up to 500 mg/l dosage there was no significant change in the sample appearance. At dosages of 1000 mg/l and above there was almost instant floc formation. However, the supernatent was still very turbid even after centrifugation. The pH at 500 mg/l dosage was 8 and those at 1000, 1500, and 2000 mg/l were 10.3, 11.1, and 11.5 respectively. The $Ca(OH)_2$ treatment was judged as ineffective.

TABLE 6. CHEMICAL FLOCCULATION SCREENING TEST RESULTS FOR WEST REFINERY SKIMMER EFFLUENT (Continued).

Raw Sample					Treatment				
Collection Date and Time	Type of Sample	Characteristics COD mg/l	pH	Temp. °F	Coagulants Type	Dosage, mg/l	Coagulant Aid Type	Dosage, mg/l	Qualitative Observations and Conclusions from Jar Test Results
--	--	--	--	--	$CaCl_2$	100 to 2000	--	--	At 200 mg/l dosage there was no apparent change. At 500 mg/l and above there was floc formation. However, the sample was still very turbid after centrifugation. In this particular the flocs floated on the top. The pH at 200 mg/l dosage was 6.9 and that at 1500 mg/l dosage was 6.2. The $CaCl_2$ treatment was judged as ineffective.
--	--	--	--	--	$Fe_2(SO_4)_3$	200 to 1500	--	--	Up to 300 mg/l dosage there were no visible flocs. The mg/l dosage formed very small flocs after a few minutes. 1000 mg/l and layer dosages gave instant flocs. However, the sample was still very turbid. Some flocs floated to the top, some settled, and some still remained in suspension throughout the depth after centrifugation. The pH at 200 mg/l dosage was 7.2 and gradually decreased to 5.7 at dosage of 1500 mg/l. The $Fe_2(SO_4)_3$ treatment was judged ineffective.
--	--	--	--	--	$Al_2(SO_4)_3$	200 to 1000	--	--	Similar results as above except that the pH at 1000 mg/l dosage was 6.5. $Al_2(SO_4)_3$ treatment was also judged ineffective.
--	--	--	--	--	$FeCl_3$	500	DOW N-11	5	Using 4 of these polyelectrolytes along with 500 mg/l $FeCl_3$ gave large flocs. However, the results were judged as no better than $FeCl_3$ treatment alone. This treatment was also judged as ineffective.
						500	DOW N-11	5	
						500	DOW N-11	5	
						500	DOW N-11	5	

TABLE 6. CHEMICAL FLOCCULATION SCREENING TEST RESULTS FOR WEST REFINERY SKIMMER EFFLUENT (Continued)

Raw Sample Collection Date and Time	Type of Sample	Characteristics COD mg/l	pH	Temp. °F	Treatment Coagulants Type	Coagulants Dosage, mg/l	Coagulant Aid Type	Coagulant Aid Dosage, mg/l	Qualitative Observations and Conclusions from Jar Test Results
9-10-69	Composite of 2 hr. grab sample over 16 hr. period.	3,900	6.2	--	$CaCl_2$	500 to 1500	--	--	There was apparent flocculation. The flocs settled; however, the supernatent was still turbid after centrifugation indicating that there was no destabilization of the emulsions. The treatment with these chemicals was judged ineffective.
					$Ca(OH)_2$	500 to 1000	--	--	
					$Al_2(SO_4)_3$	500 to 1500	--	--	
--	--	--	--	--	$FeCl_3$	500 to 1000	--	--	At these dosages flocs were observed; however, the supernatent was still turbid after centrifugation. pH at 500 mg/l dosage was 5.2 and that at 1000 mg/l was 4.6. This treatment was judged ineffective.
--	--	--	--	--	$FeCl_3$	500	DOW C-31	5	Some flocs formed. No clear supernatent after settling.
						500	DOW A-23	5	Some flocs formed. No clear supernatent after settling.
						500	DOW N-11	5	Relatively clear supernatent. However, still lot of turbidity after settling.
						500	DOW	5	Considered as less effective than DOW N-11; however, better than C-31 and A-23. The combination of 500 mg/l $FeCl_3$ and 5 mg/l of DOW N-11 marked the best in this series. COD was reduced from 3900 mg/l to 1300 mg/l. This treatment was judged as effective on this composite sample.

Flows were obtained by timing the total duration of pumping over a given time interval. Due to some difficulties in recording the flows, it was not always possible to determine the flow rates and the total flows corresponding to the time or period of sampling. Since the effectiveness of the Imhoff tank located in between the skimmer outlet and the lagoon inlet was considered negligible, no sampling was done to define its performance.

Other grab samples from the acidulation facilities, lagoon effluent and subsurface drainage were collected from sample points 3, 4, and 5, respectively. Flows for these discharges were estimated from process design requirements. Results of this survey in conjunction with data generated by ADM is presented in Section V and will not be presented here.

The wastewater survey revealed that BOD (as approximated by COD) and oils was the major problem in the effluent from the West Plant. Further, comparisons of the three major sources of wastewaters revealed that the refinery wastewaters contribute over 80% of the organic load. Consequently, emphasis was placed on the chemical/physical treatment of the refinery wastewaters for BOD_5 and oil reduction.

Since results of the analysis of lagoon effluent samples showed little, if any, equalization of other significant or consistent improvement in quality over the skimmer effluent samples, major emphasis was placed on the treatment of the refinery skimmer effluent wastewaters. Grab and 24-hour composite skimmer effluent samples obtained during the problem definition survey were evaluated to determine the most effective and economical process for reduction of BOD_5 and oils. Grab versus composite samples were tested to determine the necessity and advantages of equalization prior to further treatment. Laboratory tests included pH adjustment, activated carbon absorption, inorganic and organic chemical coagulation for emulsion destabilization, and gravity settling and air flotation for separation of chemical flocs and oils.

Coagulation screening tests were performed on grab as well as composite samples of skimmer effluent for refinery wastewater. These studies were qualitative in nature and were conducted to determine the types of coagulants best suited for the wastewater and to investigate the need for an equalization basin.

Grab Samples

Fifty-milliliter samples were used for these summary tests. Different coagulants with and without different polyelectrolytes were screened. After coagulant(s) addition, the samples were slowly stirred and observed for floc formation and supernatant clarity. The coagulant which did not form flocs in 30 minutes and/or did not produce a clear supernatant were not evaluated further. The results of these studies are presented in Table 6. Although not shown in Table 6, the results of varying wastewater pH with acid and lime did not produce a significant reduction in COD or improvement in wastewater clarity. Also tried and found not effective was the use of activated carbon--tried along, at various adjusted wastewater pH's, and in combination with several coagulants. No benefit was observed to justify the increased cost of this chemical absorbant.

It may be noted that the coagulants that worked on one grab sample (9/9/69 - 11:30 a.m.) did not work at all on the other (9/9/69 - 3:30 p.m.). Also, it may be noted that in some cases the flocs settled, and in the others they floated. These results indicate that for unequalized samples one single approach or solution may not consistently work on the skimmer effluent wastewater.

Composite Samples

At this point the same coagulants were tried on the composite samples of the skimmer effluent. The results (presented in Table 6) were very encouraging. The combination of ferric chloride ($FeCl_3$) and calcium hydroxide ($Ca(OH)_2$) seemed to produce the best and most consistent results. This treatment combination was subsequently quantitatively investigated for COD and oil removal.

Quantitative studies on coagulation were performed on seven 24-hour composite samples. These samples were obtained by continuous collection of the wastewater from the discharge side of the skimmer inlet pump. The composite samples were approximately at room temperature due to a loss of heat on standing, whereas the temperature of the wastewater going to the skimmer varied over a range of 110° to 155°F. In order to simulate composite skimmer effluent, the samples were mixed well and allowed to stand for 30 minutes and the top oil layer was skimmed off. The subnatant was used for the studies.

The results of the composite sample coagulation studies are presented in Table 7. Quantitative performance was judged on the basis of COD alone with simultaneous qualitative visual inspection of floc settleability and supernatant clarity. The results indicated that the combination of 100 mg per liter $FeCl_3$ plus 300 to 500 mg per liter $Ca(OH)_2$ generally gave the best results. Increasing the $FeCl_3$ dosage to 200 mg per liter did not give any better results. In fact, in many cases, the floc settling rate was observed to be slower.

The variability of the 24-hour composite treated skimmer effluent COD's are presented in Figure 8. These results show that for the present refinery skimmer effluent wastewater characteristics, $FeCl_3$ and $Ca(OH)_2$ coagulation followed by sedimentation would reduce COD's to equal to or less than 850 mg per liter for 50% of the samples, and equal to or less than 1,500 mg per liter for 90% of the samples. This represents approximately 65% COD reduction on the average.

At the time of these investigations no specific limits for fats, oils and greases (fat) were imposed by the municipality on the effluent. Hence, in order to avoid an excessive analytical work load on the personnel, only four samples of raw and treated skimmer effluent were analyzed for fat. The results indicated that the skimmer effluemt FOG can be substantially reduced by $FeCl_3$ and $Ca(OH)_2$ coagulation followed by gravity sedimentation. The maximum and minimum fat concentrations of the treated skimmer effluent were 266 mg per liter and 10, respectively.

TABLE 7. CHEMICAL FLOCCULATION RESULTS OF SAMPLES OF WEST PLANT REFINERY SKIMMER EFFLUENT

Date of Sampling	Hours Composited	Raw Wastewater Characteristics "COD"	Oil	pH	Chemical Dosage* $FeCl_3$ mg/l	$Ca(OH)_2$ mg/l	Treated Wastewater Characteristics "COD" mg/l	"COD" % Reduction	pH	Qualitative Observations and Conclusions from Jar Test Results
9-12-69	24	3048	2155	6.3	100	200	--	--	6.3	Very poor flocculation and very poor settling. Good flocculation. Very slow settling flocs. Treatment considered effective.
					100	300	--	--	--	
					100	400	--	--	--	
					200	200	--	--	6.2	Results no better than above. However, larger sludge volume. Treatment considered effective.
					200	300	--	68.5	6.4	
					200	400	794	73	--	
9-14-69	24	1682	635	6.5	100	200	572	66	7.2	Good flocculation, floc settling slow. Many flocs stayed in suspension. Clear supernatant.
					100	400	568	66	7.4	Almost instant floc formation. Good flocculation. Floc settling very good. Very clear supernatant. Treatment considered effective.
					100	600	620	63	7.5	
					200	200	--	--	6.7	Good flocculation. Floc settling slow. Many flocs still in suspension, clear supernatant.
					200	400	673	60	6.8	Almost instant floc formation. Good flocculation. Floc settling very good. Very clear supernatant. Flocs judged to be less dense than with 100 mg/l $FeCl_3$ + comparable $Ca(OH)_2$ dosage. Treatment considered effective.
					200	600	594	64.5	7.0	

TABLE 7. CHEMICAL FLOCCULATION RESULTS OF SAMPLES OF WEST PLANT REFINERY SKIMMER EFFLUENT (Continued)

Date of Sampling	Hours Composited	Raw Wastewater Characteristics "COD"	Oil	pH	Chemical Dosage $FeCl_3$ mg/l	$Ca(OH)_2$ mg/l	Treated Wastewater Characteristics "COD" mg/l	% Reduction	pH	Qualitative Observations and Conclusions from Jar Test Results
9-15-69	16	2523	842	6.2	100	200	846	66.5	--	Good flocculation. Floc settling slow. Clear Supernatant.
					100	300	678	73	--	Good flocculation. Floc settling very
					100	400	762	69.5	--	good. Clear supernatant.
9-16-69	24	1629	--	6.2	100	200	1051	35.6	6.7	Flocs not well defined. Poor floc-culation. Supernatant turbid.
					100	300	835	48.7	7.0	Very good flocculation. Very good
					100	400	851	47.8	7.5	flocs. Floc settling very good. Very good supernatant.
					200	200	--	--	6.6	Flocs not well defined. Poor floc-culation. Supernatant turbid.
					200	300	794	51.3	6.7	Good flocculation. Loose flocs. Floc
					200	400	867	47	6.8	settling slow. Clear supernatant.
9-17-69	24	2155	--	8.2	100	200	--	--	--	This sample was not considered normal
					100	300	--	--	--	by ADM. It rained heavily on this day.
					100	400	--	--	--	pH of raw wastewater was adjusted to 6.2
					100	500	1787	17	7.1	with addition of H_2SO_4. The oil liberated was skimmed off before conducting test. $CaC(OH)_2$ dosage of 400 mg/l and 500 mg/l along with 100 mg/l $FeCl_3$ gave good flocculation and clear supernatant. Flocs settled fast. However, COD reduction was poor.

TABLE 7. CHEMICAL FLOCCULATION RESULTS OF SAMPLES OF WEST PLANT REFINERY SKIMMER EFFLUENT (Continued)

Date of Sampling	Hours Composited	Raw Wastewater Characteristics "COD"	Oil	pH	Chemical Dosage $FeCl_3$ mg/l	$Ca(OH)_2$ mg/l	Treated Wastewater Characteristics "COD" mg/l	"COD" % Reduction	pH	Qualitative Observations and Conclusions from Jar Test Results
9-18-69	24	4993	--	5.6	100	200	--	--	--	Flocculation test gave negative results.
					100	400	--	--	--	Flocs were almost throughout the depth.
					100	600	4047	19	7.1	No settling, no flating of flocs.
					100	800	--	--	--	Dow N-11 at 1 to 2 mg/l dosage along with those coagulants also did not help.
9-19-69	24	2050	266	5.8	100	300	783	61.5	6.2	Small flocs. Slightly turbid supernatant. Floc settling good.
					100	400	804	61	7.0	Small flocs. Clear supernatant. Floc settling very good.
					100	500	840	59	8.2	
					100	600	--	--	8.3	

*Flocculation Procedure: 500-ml sample in 1 liter beaker, chemical added; 2 minutes rapid mix at 100 rpm; 15 minutes flocculation at 40 rpm; supernatant analyzed after 15 minutes settling.

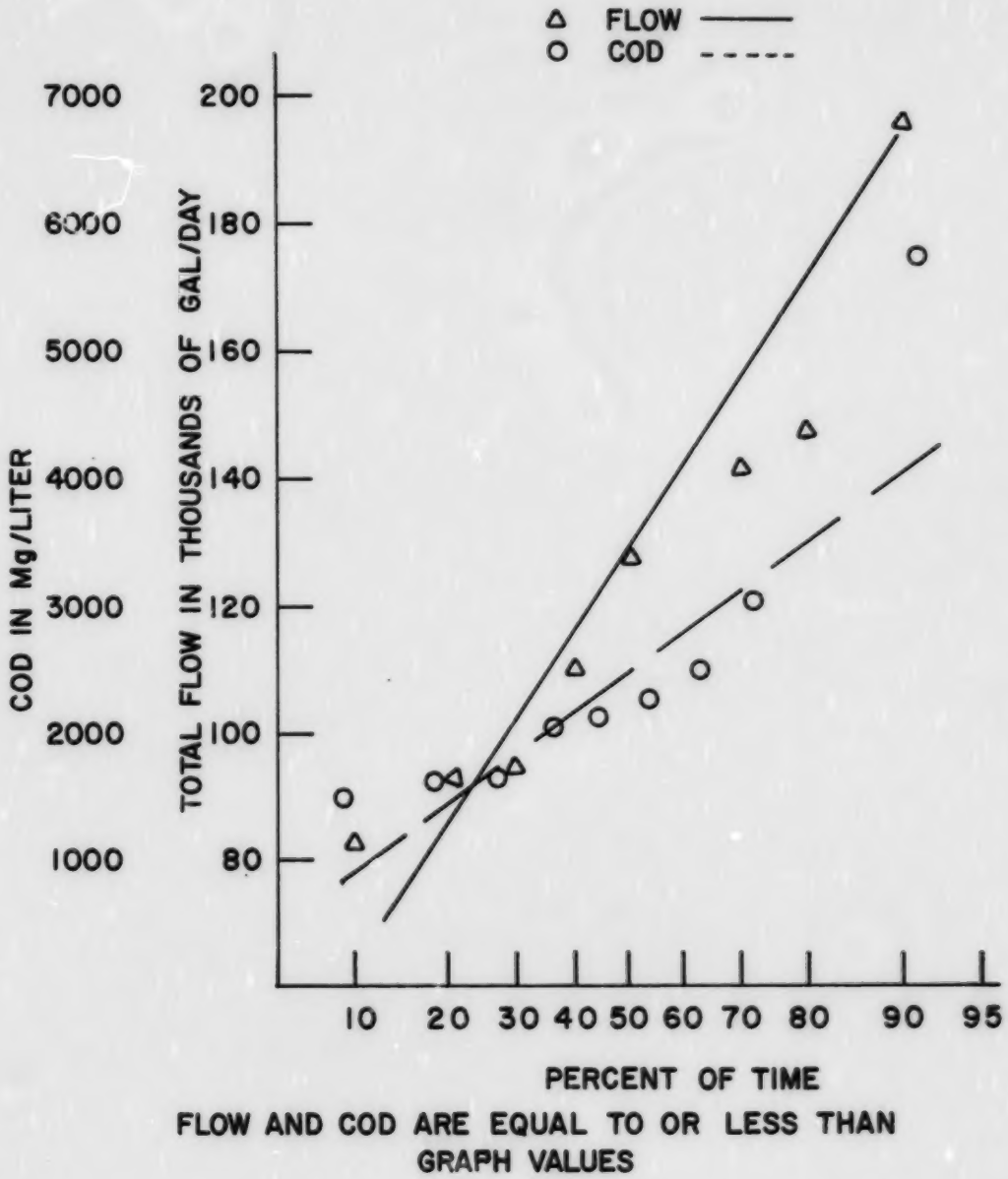


Figure 8. West plant refinery skimmer effluent variability of 24 hr composite COD and flows.

TABLE 8. LABORATORY SETTLING TEST RESULTS OF REFINERY SKIMMER EFFLUENT

Collection Date (Ending)	24-hr Composite Sample* COD, mg/l	Oil, mg/l	Treatment Coagulant $FeCl_3$, mg/l	Dosage $Ca(OH)_2$, mg/l	Laboratory+ Overflow Rate gas/sq ft/day	Settled Supernatant Quality‡ COD mg/l	COD % reduction	Oil mg/l	Oil % reduction	Suspended Solids and Sludge Production Sludge Volume ml/l of Waste	Suspended Solids after Chemical Treatment, mg/l	Remarks and Observations
9-13-69	3,048	2,155	100	400	1,200	1,314	57	--	--	70	904	Clear supernatant. Turbidity judged as 10 Jackson Turbidity Units (JTU).
					600	946	69	--	--	65		
					400	998	67	266	87	50		
					200	1,050	65.5	--	--	50		
9-14-69	1,682	635	100	400	400	557	67	97	85	43	622	Visual inspection of the suspension during the test indicated that similar removal could be obtained at overflow rates of 600 gpd/sq ft. Clear supernatant.
9-15-69	2,523	848	100	400	400	778	69	131	85	60	884	
9-17-69	2,155	--	100	500	200	1,734	19.5	--	--	105	922	
9-19-69	2,050	266	100	400	1,200§	840	59	--	--	105	--	Clear supernatant. Turbidity judged as 10 JTU.
					600	820	60	--	--	80	--	
					400	825	59.5	10	96	65		
					300	794	61	--	--	57	--	
					125	778	62	--	--	43	--	

*Samples were pretreated in the settling cylinder itself, using the indicated coagulant dosages and flocculated for 15 minutes prior to settling. These coagulant dosages were judged as optimum by jar test analysis. The samples were at room temperature.

+One-Liter graduated cylinder settling test, (14" water depth).

§Six-Liter cylinder settling test, (14" water depth).

‡In all the tests a thin scum layer was observed floating on the top. This was excluded from the supernatant sample.

A series of laboratory-scale settling tests were performed at room temperature using skimmer effluent wastewater treated with the optimum coagulant dose of ferric chloride and calcium hydroxide (determined by a modification of the previously described screening procedure). A summary of results is presented in Table 8. A small percentage of solids floated to the liquid surface in all the coagulation and sedimentation studies, indicating the need for some type of skimming equipment in the clarifier.

The relationship between clarification overflow rate and the treated effluent COD is presented in Figure 9. Generally, suspended solids removal is used as a criteria in determining the design overflow rate for a sedimentation tank. However, in this particular case, with the removal of flocculated wastewater BOD_5 being the prime consideration, supernatant COD was used as a criteria to determine the overflow rate. The data shown in Figure 9 is typical of the several settling tests run and is summarized in Table 8. Interpretation of the laboratory overflow rates indicated that in most cases a clarifier overflow rate of approximately 750 gal per square foot per day will produce an effluent with a minimum COD. A scale up adjustment factor of 1.5 was applied to the laboratory observed overflow rate to account for hydraulic turbulence, temperature induced turbulence, inlet and outlet losses, etc. In one case the floc settling was very rapid and a laboratory overflow rate as high as 1200 gal per square foot per day also produced very good supernatant. For design purposes, however, an adjusted overflow rate of 500 gal per square foot per day was used.

The effectiveness of chemical coagulation of grab samples taken from the skimmer outlet at different times of day was not consistent, indicating that effective equalization is necessary for reliable treatment. The chemical coagulation of 24-hour composite samples from the skimmer effluent, in most cases, gave good results, indicating that 24-hour equalization should be sufficient.

Chemical coagulation of equalized skimmer effluent (using a combination of ferric chloride and calcium hydroxide) followed by flocculation and sedimentation reduced the COD to 850 mg per liter or less in 50% of the samples and to about 1,500 mg per liter or less in 90% of the samples. The behavior of two samples taken on September 17 and 18, 1969 stresses the importance and the need for dependable in-plant treatment with calcium chloride, and effective oil separation and removal in the new in-plant and the existing refinery wastewater effluent skimmers. A summary of the investigative results is given in Table 9.

TABLE 9. SUMMARY OF INVESTIGATIVE RESULTS

Item	Amount
Equalization:	
Detention Time, Hours	24

TABLE 9. SUMMARY OF INVESTIGATIVE RESULTS (Continued)

Item	Amount
Coagulation:	
Ferric Chloride ($FeCl_3$) Dose, mg/l	100
Calcium Hydroxide ($Ca(OH)_2$) Dose, mg/l	
Minimum, mg/l	300
Average, mg/l	400
Maximum, mg/l	500
Clarification:	
Overflow Rate (lab), gal/sq ft/day	500
Average COD Reduction, %	65
Average Fat, Oils, and Greases Reduction, %	85
Treated Effluent:	
COD, mg/l, 50% Probability Value	850 (1,300)*
90% Probability Value	1,500 (2,200)
Fats, Oils, and Greases, mg/l	10-270 (10-400)
Clarifier Sludge	
Minimum Solids Concentration, %	1
Maximum Solids Concentration, %	2
Average Sludge Production, % of Wastewater Flow	6

*Figures in parenthesis indicate future production rate.

General Basis of Design and Recommended Process

The design of the treatment facilities is based on the estimated 90% probability-of-occurrence value of future West Plant refinery skimmer effluent flows and loadings. Chemical dosages are based on the results of laboratory investigations using compsited skimmer effluent samples. A scale-up factor of 1.5 has been applied to the results of laboratory overflow rates to obtain design overflow rates for the clarifiers. Flocculator-clarifier units are provided in duplicate for maintenance and operating flexibility.

The design of chemical feed systems is based on the requirement that minimum supervision and operating manpower will be available. Hydrated lime, instead of pebble lime, will be used. However, since the average lime requirement is only 725 lb per day as $Ca(OH)_2$, the additional cost of hydrated lime over pebble lime is negligible. The capacities of the lime feeder, lime mixing tank, and transfer pumps are designed such that a whole day's lime slurry requirement can be prepared in one to two hours during the day shift. The lime slurry storage tank is designed to store three days' average supply of lime

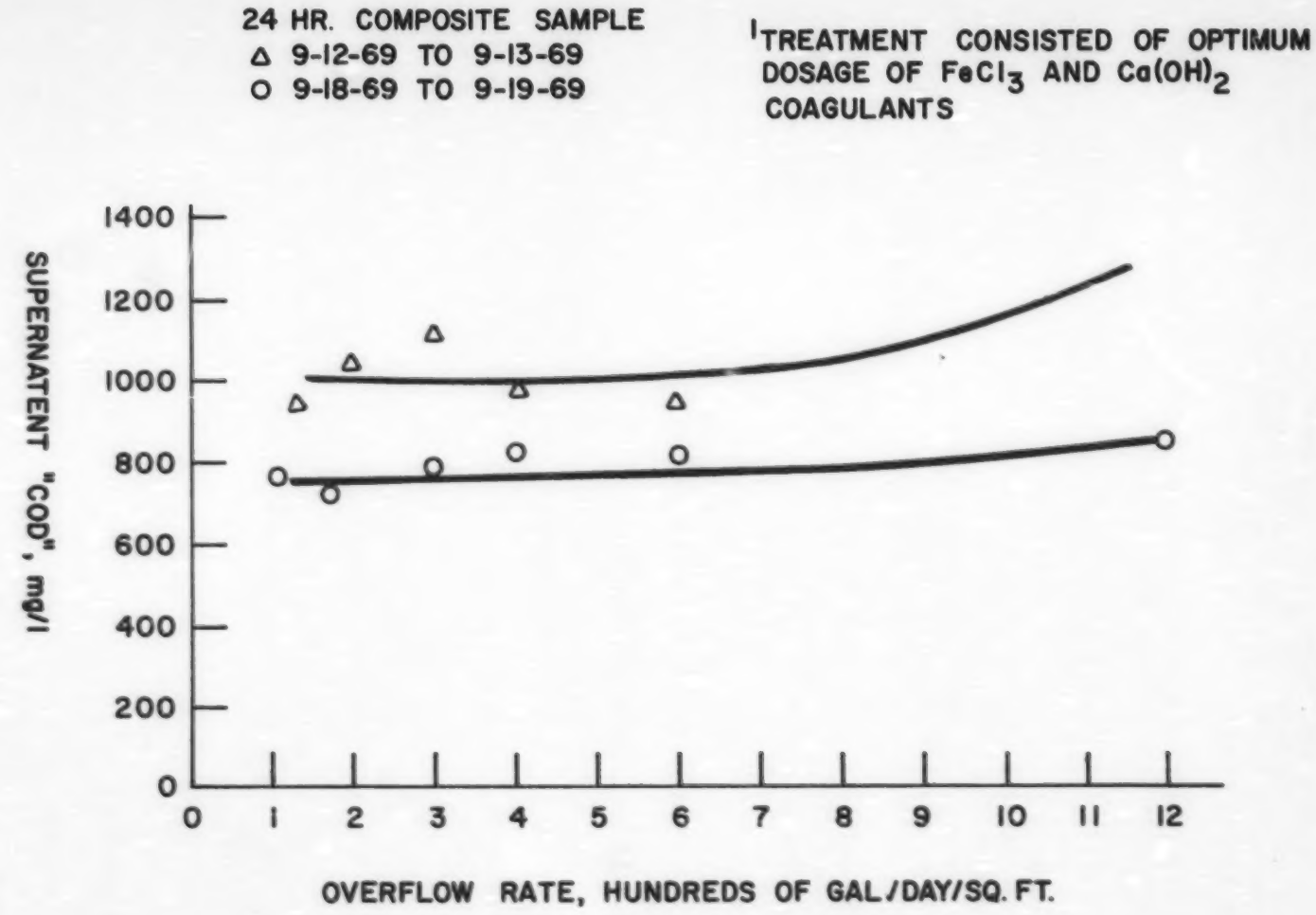


Figure 9. West plant refinery treated skimmer effluent settling test results.

at a 10% slurry concentration. This will also allow the storage of weekend lime slurry feed requirements, and thereby minimize operator attention over the weekend. The capacity of the lime dry storage hooper is designed for 1.5 times the capacity of a delivery truck. This provides approximately 15 days' storage at the average rate of use.

Ferric chloride will be purchased, stored, and fed in liquid form. Acid resistant materials will be used through this system.

Equalization of skimmer effluent is necessary to level out the variability of flows and loadings prior to chemical treatment, as was demonstrated during the treatability survey. A portion of the existing lagoon will be modified to serve as the equalization basin. The remainder of the existing lagoon will provide a second basin to serve as emergency storage for excessive surface runoff, production leaks, and spills and other miscellaneous flows. These accumulated wastewaters will be bled into the equalization basins for further treatment prior to discharge to the municipal sewer system.

The design assumes that the necessary changes in the refinery effluent pumping and skimming facilities, as previously discussed, will be completed, and that these units will remain as part of the proposed treatment scheme. The present Imhoff tank and lagoon will be abandoned or modified for use in proposed new treatment facilities. Since the refinery wastewaters are presently receiving $CaCl_2$ treatment, no further adjustments were made to account for the changes when this treatment is moved in-plant.

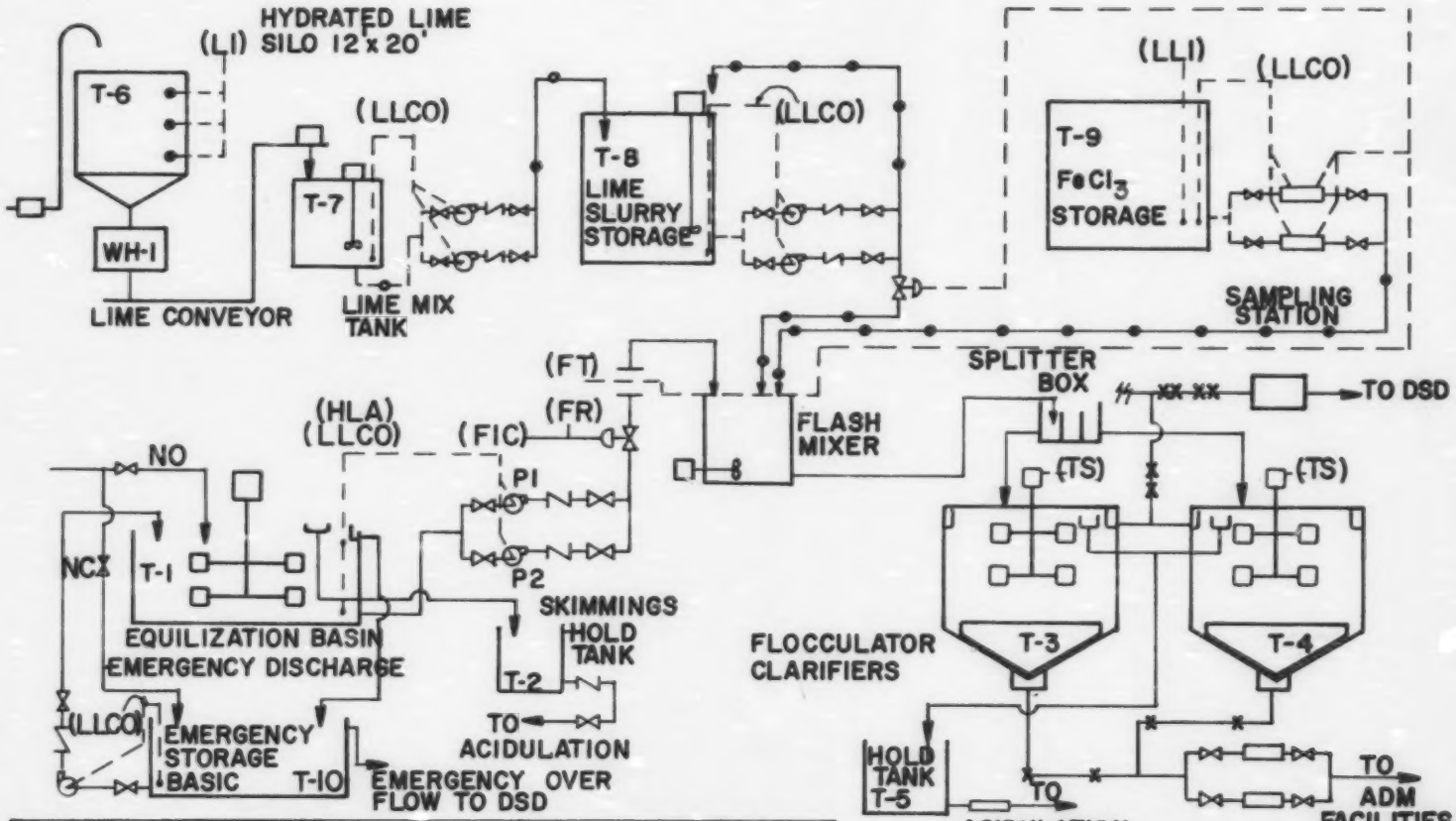
Description of Proposed Facilities

The schematic flow diagram for the proposed treatment facilities and the preliminary plot plan are shown in Figure 10.

The wastewater from various refinery sources after being collected in the existing sump, will be pumped to the existing skimmer, where free floating oil present in the wastewater will be removed. The skimmer effluent will then flow by gravity to the equalization basin (T_1), which will provide an equalization period of one day at design flows. Manually-diverted influent or any overflow from the equalization basin will be stored in an emergency storage basin (T_{10}) with a capacity of 180,000 gal and will be pumped back (via Pump P_{13}) to the equalization basin at a manually controlled rate during the periods of low in-flows, for retreatment. Under normal conditions, the emergency basin will remain empty.

The equalized skimmer effluent will be pumped (using two centrifugal pumps, P_1, P_2) to the flash mix tank.

A constant flow rate, adjusted manually according to the level in the equalization basin, insures more uniform operation and performance of the downstream facilities, and simplifies control of the coagulants feeding systems. Lime and ferric chloride will be added automatically in proportion to the wastewater flow. Lime will be fed from a recirculated storage tank system with a flow-activated control valve. Ferric chloride solution will be fed directly



HLA	HIGH LEVEL ALARM	LI	LEVEL INDICATOR
LLCO	LOWLEVEL CUT OFF	LLI	LOW LEVEL INDICATOR
FR	FLOW RECORDER	NC	NORMALLY CLOSED
FT	FLOW TOTALIZER	NO	NORMALLY OPEN
FIC	FLOW INDICATOR CONTROLLER		
TS	TORQUE SWITCH		

Figure 10. Proposed treatment facility.

from the storage tank by a variable-speed metering pump controlled by the wastewater flow. The lime and ferric chloride feed systems will be housed in a small control building. The lime storage bin will be located outside the building.

From the flash mixer, the wastewater will then flow by gravity through a flow splitter box to two 25-foot diameter flocculator-clarifiers, where the coagulated wastewater will be flocculated by gentle stirring in the flocculation zone before being settled in the outer clarification zone. The clarifier effluent will then flow by gravity to the existing sewer leading to the municipal sewer system. The clarifier sludge will be raked to the center wells of the flocculator-clarifier units and pumped to sludge handling facilities to be provided by ADM.

The skimmings collected from the equalization basin and the flocculator-clarifiers will be pumped separately using two positive displacement pumps (P_3, P_6) to the acidulation facilities. Separate handling and use of progressive-cavity pumps are proposed to minimize plugging during winter months due to the hardening of the skimmer oils.

TABLE 10. SUMMARY OF DESIGN BASIS AND MAJOR UNIT SIZES

General Design Basis	Probability of Occurrence 50%	90%
Refinery Skimmer-Effluent:		
Flow, gpd	195,000	293,000
COD, mg/l	4,000	6,400
COD, lb/day	6,500	12,000
Population Equivalent	38,000	70,000
Fats, Oils, and Greases, mg/l	1,550	*
Fats, Oils, and Greases, lb/day	2,500	*
Expected Treated Refinery Effluent:		
COD, mg/l	1,300	2,200
COD, lb/day	2,100	4,200
Population Equivalent	12,500	25,000
Fats, Oils, and Greases, mg/l	300	*
Fats, Oils, and Greases, lb/day	500	*
Estimated Total West Plant Effluent:		
COD, mg/l	700	1,200
COD, lb/day	2,500	4,700
Population Equivalent	15,000	28,000
Fats, Oils, and Greases, mg/l	220	*
Fats, Oils, and Greases, lb/day	740	*

TABLE 10. SUMMARY OF DESIGN BASIS AND MAJOR UNIT SIZES (Continued)

General Design Basis	Probability of Occurrence 50%	90%
Estimated Sludge Production:		
lb/day	1,350	2,000
Percent Solids	1.5	1.5
gal/day	11,000	16,000
Chemical Consumption:		
Lime, lb/day	725	1,100
gal/day at 10%	875	1,300
$FeCl_3$, lb/day	160	240
gal/day at 40%	500	725

*Insufficient data available to calculate.

TABLE 11. SUMMARY OF MAJOR EQUIPMENT SIZES

Item	Amount
Equalization Basin, T_1:	
Number	One
Dimensions	50' X 50' X 18' deep (16' SWD)
Capacity	300,000 gal (40,000 cu ft)
Detention Time	24 hours at 90% probable flow
Mixer, M-1	One 15-HP platform-mounted
Materials of Construction	(Existing lagoon will be modified sheet pile, side walls, and concrete lined bottom
Effluent Pumps (P_1, P_2):	
Number	Two (one alternating standby)
Type	Non-clog, centrifugal
Capacity	250 gpm at required TDH
Control	Manual, liquid-level override
Skimmings Holding Tank (T_2):	
Number	One
Capacity	1000 gal

TABLE 11. SUMMARY OF MAJOR EQUIPMENT SIZES (Continued)

Item	Amount
Skimmings Pump (P_3):	
Number	One
Capacity	50 gpm
Type	Positive-displacement, progressive cavity
Control	Liquid-level in skimmings tank
Flocculator-Clarifiers (T_2, T_3):	
Number	Two
Required Flocculation Zone Detention Time	20 minutes at 90% probable flow
Dimensions	8' diameter X 6' height
Design Overflow Rate for Settling Zone	500 gal per sq ft per day
Detention Time in Clarifier Zone	5 1/2 hours at 90% probable flow
Overall Dimensions	25' diameter X 14' deep (includes 2' freeboard plus 2' sludge zone)
Volume of Each Unit	6,900 cu ft or 51,500 gal
Material of Construction	Steel
Sludge and Scum Collection	Units provided with surface skimmer, sludge raked to center well
Sludge Pumps (P_4, P_5):	
Number	Two (one alternating standby)
Type	Positive-displacement, progressive-cavity
Capacity	50 gpm at required TDH
Control	Time controlled, constant speed
Skimmings Pump (P_6):	
Number	One
Type	Positive-displacement, progressive-cavity
Capacity	50 gpm at required TDH
Control	Liquid-level in skimmings tank
Lime Feed Facilities (T_6):	
Lime Storage Bin:	
Number	One
Capacity	30 tons of hydrated lime, or 75 days at normal feed rate

TABLE 11. SUMMARY OF MAJOR EQUIPMENT SIZES (Continued)

Item	Amount
Volume	1,500 cu ft
Material of Construction	Steel
Material Stored	Hydrated lime
Lime feeder:	
Number	One
Capacity	800 lb per hour
Type	Volumetric
Mixing Tank (T_7):	
Number	One
Volume	1450 gal or 190 cu ft
Dimensions	7' diameter X 7'depth (5' SWD)
Volume of Each Unit	6,900 cu ft or 51,500 gal
Material of Construction	Steel
Sludge and Scum Collection	Units provided with surface skimmer, sludge raked to center well
Sludge Pumps (P_4, P_5):	
Number	Two (one alternating standby)
Type	Positive-displacement, progressive-cavity
Capacity	50 gpm at required TDH
Control	Time controlled, constant speed
Skimmings Pump (P_6):	
Number	One
Type	Positive-displacement progressive-cavity
Capacity	50 gpm at required TDH
Control	Liquid-level in skimmings tank
Lime Feed Facilities (T_6):	
Lime Storage Bin:	
Number	One
Capacity	30 tons of hydrated lime, or 75 days at normal feed rate
Volume	1,500 cu ft
Material of Construction	Steel
Material Stored	Hydrated lime
Lime Feeder:	
Number	One
Capacity	800 lb per hour
Type	Volumetric

TABLE 11. SUMMARY OF MAJOR EQUIPMENT SIZES (Continued)

Item	Amount
Mixing Tank (T_7):	
Number	One
Volume	1450 gal or 190 cu ft
Dimensions	7' diameter X 7' depth (5' SWD)
Lime Slurry Concentration	10%
Mixer, M-2	One at 3 HP
Material of Construction	Steel
Lime Slurry Transfer Pumps (P_7, P_8):	
Number	Two (one alternating standby)
Type	Non-clog, centrifugal
Capacity	50 gpm at required TDH
Control	Manual
Lime Slurry Storage Tank (T_8):	
Volume	3,500 gal or 467 cu ft
Dimensions	9' diameter X 10' deep (8' SWD)
Storage Capacity	2,400 lb of lime or 3 days at normal feed rate
Mixer, M-3	One at 2 HP
Material of Construction	Steel
Lime Slurry Feed Pumps (P_9, P_{10}):	
Number	Two (one alternating standby)
Type	Non-clog centrifugal
Capacity	10 gpm at required TDH
Control	Flow rate from equalization basin effluent
Ferric Chloride Feed System:	
Storage Tank (T_9):	
Number	One
Capacity	10,000 gal or 1,430 cu ft or 24 days at normal feed rate
Dimensions	14' diameter X 10' deep
Material of Construction	Steel tank with acid-resistant lining
Material stored	40% ferric chloride solution
Ferric Chloride Feed Pumps: (P_{11}, P_{12})	
Number	Two (one alternating standby)
Type	Positive-displacement pump

TABLE 11. SUMMARY OF MAJOR EQUIPMENT SIZES (Continued)

Item	Amount
Capacity	0-40 gph
Control	Flow rate of equalization basin effluent
Material of Construction	Acid-resistant
Emergency Storage Basin (T_{10}):	
Number	One
Dimensions	50' X 30' X 18' deep (SWD)
Capacity	180,000 gal
Materials of Construction	(Existing lagoon will be modified) sheet pile side walls, and concrete lined bottom
Emergency Pump (P_{13}):	
Number	One
Type	Non-clog, centrifugal
Capacity	250 gpm
Control	Manual, liquid-level override

Cost Estimate for Ferric Chloride and Lime Treatment with Clarification

Preliminary estimates of the construction and annual (fixed and operating) costs for the proposed wastewater treatment facilities are shown in the following tabulations. The total construction cost included a construction contingency, but excluding engineering design costs, is estimated to be $393,000. The total annual cost, including operating costs (labor, maintenance, utilities, and chemicals) and fixed cost (depreciation, interest, insurance, and taxes) is estimated to be $100,300.

TABLE 12. SUMMARY OF CONSTRUCTION COSTS*

Item	Amount
Equalization Basin	$54,000
Flocculator-Clarifiers	95,000
Lime Feed System	19,000
Emergency Storage Basin	32,000
Skimming Tanks	6,000
Control and Chemical Building	40,000

TABLE 12. SUMMARY OF CONSTRUCTION COSTS* (Continued)

Item	Amount
Subtotal	258,000
Piping (at 15%)	37,000
Electrical (at 10%)	26,000
Instrumentation (at 6%)	16,000
Site Work	5,000
Subtotal	342,000
Construction Contingency (15%)	51,000
Total Construction Costs	393,000

*Based on 1969 construction prices.

TABLE 13. SUMMARY OF ANNUAL ESTIMATED COSTS*

Item		Amount
Operating Costs:		
Labor Cost at $5.00/hr, 8 hrs/day, 260 days/hr		$10,400
Maintenance		
Mechanical	at 7% of $ 65,000	4,500
Structures	at 2% of $168,000	3,400
Electrical and Instruments	at 7% of $ 42,000	2,900
Chemicals:		
Lime, 135 tons/yr at $26.00/ton		3,500
Ferric Chloride, 30 tons/yr at $80.00/ton		2,400
Utilities:		
Electrical at 0.015/KWH, 700 KW-hr/day		4,000
Total Operating Costs		31,100

TABLE 13. SUMMARY OF ANNUAL ESTIMATED COSTS*
(Continued)

Item	Amount
Fixed Costs:	
Depreciation (18 years straight line)	22,000
Interest (10%)	39,300
Insurance and Taxes (2%)	7,900
Total Fixed Costs	69,200
Total Annual Costs	100,300

*Costs are rounded to nearest $100, 1969 prices.

SECTION VIII

DESCRIPTION AND EVALUATION OF INSTALLED WASTEWATER MANAGEMENT FACILITIES

Process evaluation was done for the equipment in Decatur. Figure 11 is a flow diagram for the treatment facilities. Flows and concentration are approximate and are based upon operating records.

FACILITIES AT DECATUR WEST PLANT

It was decided by ADM to install one 186,000-gal clarifier at the Decatur West Plant. It was felt that this clarifier along with process modifications described below would bring the waste strength to within acceptable limits. If this was unsuccessful, the process recommended by the consultant could be installed incorporating this clarifier. This was successful, so the ferric chloride and lime flocculation system was not installed.

1. Condensate Recycle: The condensate generated in the refinery, while not having any BOD, contributes a significant hydraulic load to the treatment facility. Therefore, this water was recycled for use in refining and water wash. Because of this, there was no net increase in hydraulic load as production increased resulting in longer residence time in the treatment facility. Water recycled is approximately 50,000 gallons per day.

2. Soapstock Concentration: It was found that far too much flush water was being used on the refining centrifuges. This resulted in soapstock with moisture in the 80% to 90% range. This caused the acidulation facilities to be overloaded and resulted in poor splitting due to inadequate reaction time. By simple external piping modifications, the soapstock moisture was decreased to 30% to 50%. This gave a residence time sufficient to treat the soapstock and resulting acid liquor even after expansion. The water eliminated from the waste stream was at least 50,000 gallons per day.

3. Oil Spills and Malfunctions: Projects were undertaken to eliminate possibilities of oil losses due to malfunctions. All areas where the possibility of an oil spill existed were piped to the calcium chloride treatment system. Each vacuum vessel which could overflow to the barometric cooling tower via the ejector system was equipped with high level alarms.

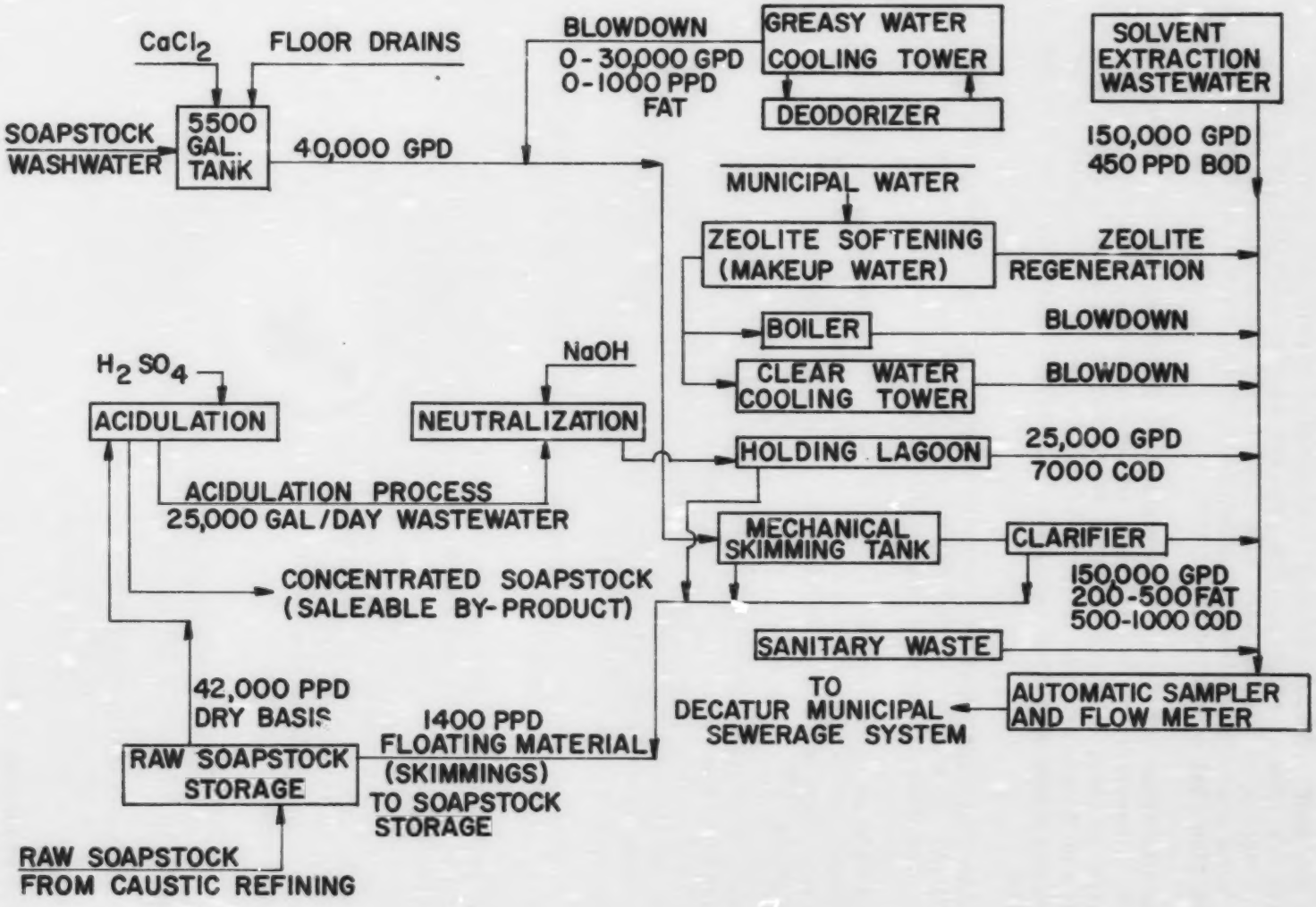


Figure 11. Decatur wastewater treatment facility.

It has been difficult to obtain meaningful operational data on the clarifier for several reasons. The refinery started refining corn oil weekly at approximately the same time the clarifier was put into operation. It was found that the wastewater generated by this process was more difficult to treat than that generated by soybean oil.

The clarifier offset the high sewer load generated by the refining of corn oil. Therefore, it is difficult to make a meaningful before and after comparison in terms of overall load. Reduction in COD will be given for a particular treatment step in terms of before and after treatment, as well as a net per pound processed reduction in strength after the clarifier was installed.

Waste treatment facilities consist of chemical flocculation equipment, a 30,000 gal skimmer, a 150,000 gal holding lagoon and a clarifier. Figure 12 is a plot plan of the existing treatment area at Decatur.

The calcium chloride treatment system is described in Section VI. All refinery wastewater and floor washings are treated in this system. As can be seen from Table 3 of Section VI, this system reduces the COD by approximately 92%.

Table 14 presents lb BOD_5 and lb fat per pound oil processed data from April 1969 to June 1974. The calcium chloride treatment was started in October 1969. This data is presented in Figures 13 and 14 with significant elements of the treatment research and installation noted. Fat analysis was not done by the city before 1970. BOD_5 and fat analysis for October, November, and December 1970 were not available.

The refinery was down due to a fire November 1969, and expanded production resumed April 1970.

Table 15 presents population equivalents, oil processed and lb BOD_5 and fat per pound of oil processed for the six month period before the calcium chloride treatment was installed and the six month period after the expanded refinery was started. There was a net reduction of 71% of the BOD_5. No fat tests were run before the calcium chloride treatment was started because the City of Decatur did not require them at that time. The last part of Table 13 is for 1973 after the clarifier was installed and all process modifications were made. BOD_5 and fat reductions for each process are summarized as follows:

Before Treatment:

.0135 lb BOD per lb OIL processed
.0041 lb FAT per lb OIL processed, estimated

After Calcium Chloride Treatment:

.0039 lb BOD per lb OIL processed
.00099 lb FAT per lb OIL Processed

71% reduction in BOD

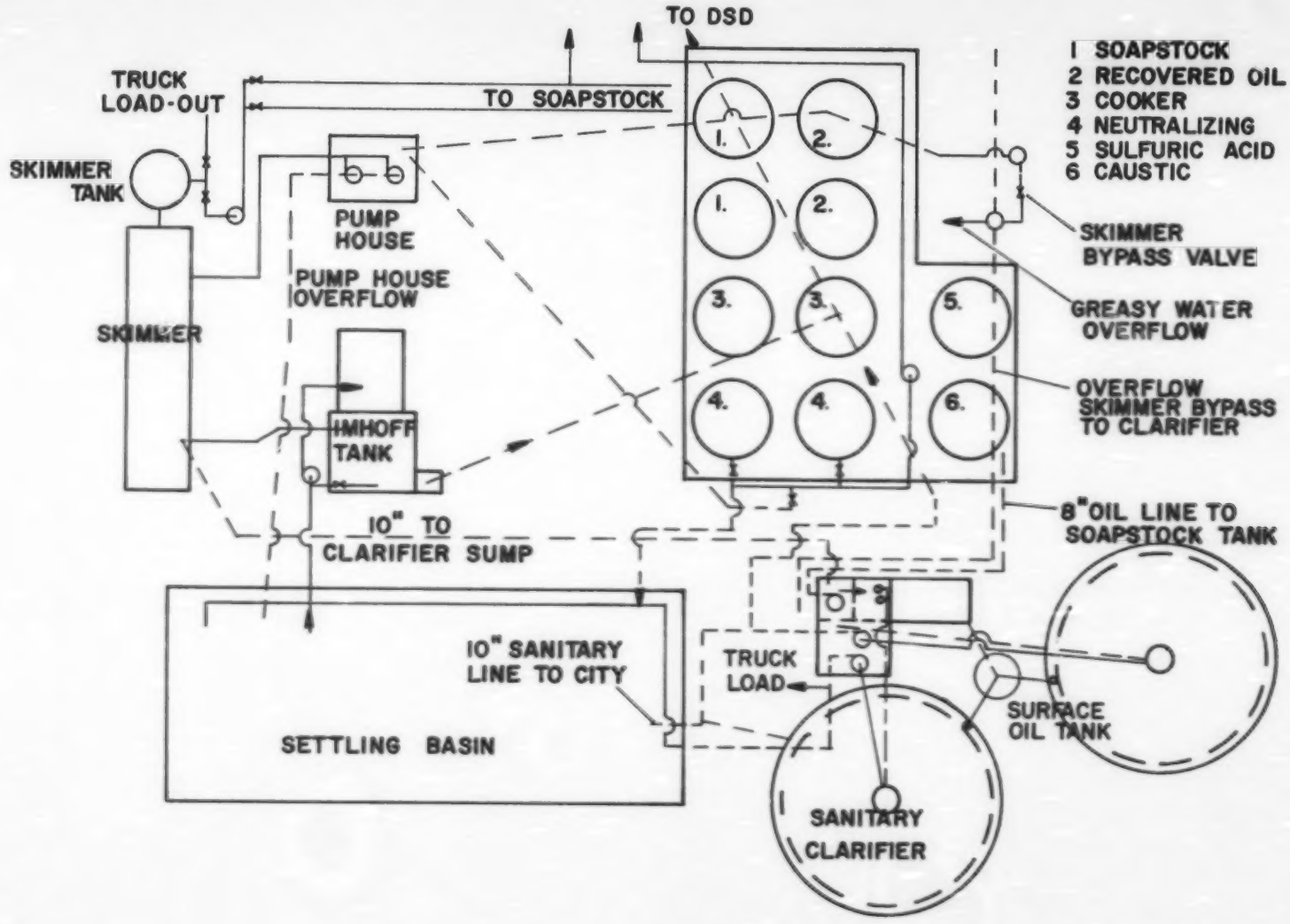


Figure 12. West plant treatment flow diagram.

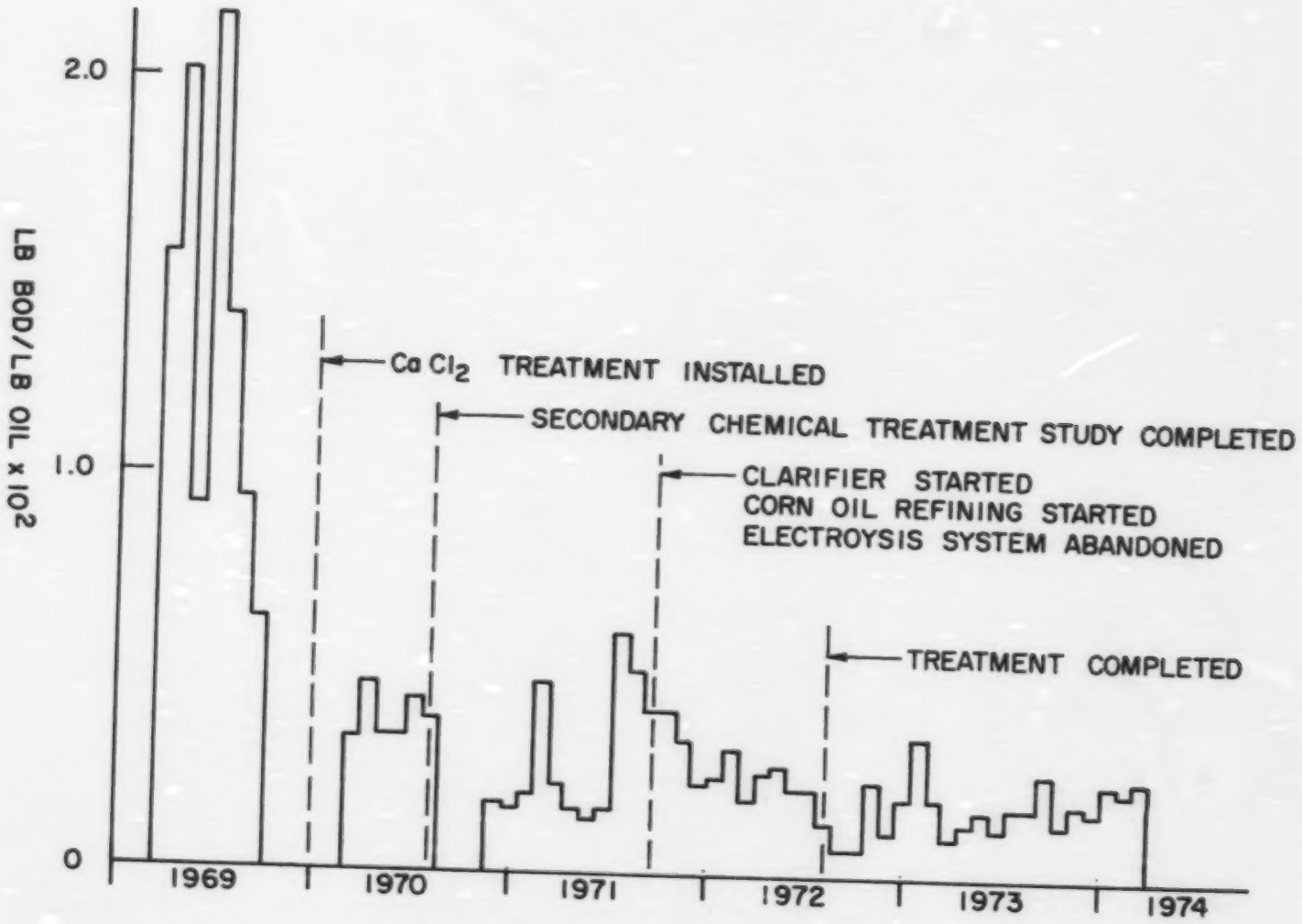


Figure 13. Pounds BOD per pound oil processed.

Figure 14. Pounds fat per pound oil processed.

After Total Treatment System:
.0019 lb BOD per lb OIL processed
.00050 lb FAT per lb OIL processed

51% reduction in BOD over primary chemical treatment
50% reduction in FAT over primary chemical treatment

86% overall BOD reduction
86% probable FAT reduction
= .0036 lb per lb processed

The clarifiers and system modifications resulted in a further reduction of 50% of the BOD_5 and fat per pound processed. The overall reduction in BOD_5 was 86%. This is probably close to the overall fat reduction for the system based on the overall reduction in the second step.

From the primary chemical treatment, the calcium chloride treatment effluent gravity flows to a sump where it is mixed with barometric condenser cooling tower overflow and surface water from the acidulation area and pumped to the skimmer. The skimmer has a volume of 30,000 gal and is diagrammed in Figure A-2 of Appendix A. The skimmer retains any oil spilled in acidulation and some additional floc from the calcium chloride treatment system. All skimmings go to acidulation.

TABLE 14. WEST PLANT EFFLUENT ANALYSIS*

Month	Oil Production, lb/day	BOD, lb/day	Fat, lb/day	lb BOD/ lb Oil Processed	lb FAT/ lb Oil Processed
Apr. 1969	407,000	6,331	--	.0155	--
May	407,000	8,186	--	.0201	--
Jun.	407,000	3,281	--	.0081	--
Jul.	409,000	8,874	--	.0217	--
Aug.	348,000	4,845	--	.0139	--
Sep.	490,000	4,420	--	.0090	--
Oct.+	339,000	2,159	--	.0063	--
Nov.+	--	--	--	--	--
Dec.	--	--	--	--	--
Jan. 1970	--	--	--	--	--
Feb.	--	--	--	--	--
Mar.	--	--	--	--	--
Apr.	603,000	2,040	893	.0034	.00150
May	726,000	3,417	448	.0047	.00062

TABLE 14. WEST PLANT EFFLUENT ANALYSIS* (Continued)

Month	Oil Production, lb/day	BOD, lb/day	Fat, lb/day	lb BOD/ lb Oil Processed	lb FAT/ lb Oil Processed
Jun.	803,000	2,703	587	.0034	.00073
Jul.	852,000	3,026	599	.0035	.00070
Aug.	829,000	3,536	1,066	.0043	.00128
Sep.	660,000	2,567	722	.0039	.00109
Oct.	1,043,000	--	-	--	--
Nov.	712,000	--	--	--	--
Dec.	788,000	--	--	--	--
Jan. 1971	895,000	1,480	460	.00165	.000514
Feb.	963,000	1,534	650	.00159	.000675
Mar.	845,000	1,640	699	.00194	.000827
Apr.	930,000	4,450	2,479	.00478	.002660
May	1,130,000	2,470	633	.00219	.000560
Jun.	915,000	1,480	427	.00162	.000466
Jul.	1,101,000	1,596	600	.00145	.000545
Aug.	1,208,000	1,994	741	.00165	.000613
Sep.	792,000	5,142	2,157	.00649	.002723
Oct.	801,000	3,900	785	.00487	.000980
Nov.	696,000	2,926	590	.00420	.00084
Dec.	868,000	3,593	1,124	.00414	.001295
Jan. 1972	1,020,000	3,450	1,149	.00338	.001130
Feb.	958,000	2,188	375	.00228	.000390
Mar.	1,118,000	2,688	557	.00240	.000498
Apr.	920,000	3,117	1,523	.00339	.001650
May	1,107,000	2,156	402	.00195	.000363
Jun.	872,000	2,338	818	.00268	.000938
Jul.	753,000	2,034	652	.00270	.000866
Aug.	635,000	1,414	807	.00223	.001270
Sep.	854,000	1,921	864	.00225	.001011
Oct.	705,000	1,089	303	.00154	.000430
Nov.	1,262,000	892	330	.00071	.000261
Dec.	1,046,000	764	226	.00073	.000216
Jan. 1973	742,000	1,836	241	.00250	.000320
Feb.	1,021,000	1,156	139	.00110	.000140
Mar.	987,000	1,887	472	.00190	.000480
Apr.	1,047,000	3,757	517	.00360	.000490
May	861,000	1,683	568	.00190	.000660
Jun.	980,000	952	183	.00100	.000190
Jul.	835,000	1,156	430	.00140	.000520
Aug.	729,000	1,1224	228	.00170	.000310

TABLE 14. WEST PLANT EFFLUENT ANALYSIS* (Continued)

Month	Oil Production, lb/day	BOD, lb/day	Fat, lb/day	lb BOD/ lb Oil Processed	lb FAT/ lb Oil Processed
Sept.	733,000	935	424	.00130	.000580
Oct.	942,000	1,700	559	.00180	.000590
Nov.	900,000	1,632	496	.00180	.000550
Dec.	1,048,000	2,856	1,217	.00270	.001160
Jan. 1974	1,030,000	1,525	437	.00148	.00420
Feb.	1,294,000	2,535	820	.00196	.000630
Mar.	1,089,000	1,904	529	.00175	.000490
Apr.	1,074,000	2,740	730	.00255	.000680
May	1,167,000	2,671	645	.00229	.000550
Jun.	1,363,000	3,420	786	.00251	.000580

*Total effluent approximately 300,000 to 400,000 GPD through grant period.
+Down for refinery fire.

TABLE 15. DECATUR WEST PLANT BOD_5 AND FAT PER POUND OF OIL PROCESSED

Month	Avg. Population Equiv.	FAT, lb/day	BOD, lb/day	Oil Production/day, lb	lb BOD/ lb Oil	lb FAT/ lb Oil
Apr. 1969	37,200		6,331	407,000	.0155	
May	48,100		8,186	407,000	.0201	
Jun.	19,300		3,281	407,000	.0081	
Jul.	52,200		8,874	409,000	.0217	
Aug.	28,500		4,845	348,000	.0139	
Sep.	26,000		4,420	490,000	.0090	
Oct.	12,700		2,159	339,000	.0063	
Nov.	3,100					
Dec.	8,400					
Calcium chloride treatment started						
Jan. 1970	5,800					
Feb.	6,600					
Mar.	13,900					

TABLE 15. DECATUR WEST PLANT BOD_5 AND FAT PER POUND OF OIL PROCESSED (Continued)

Calcium chloride treatment started

Month	Avg. Population Equiv.	FAT, lb/day	BOD, lb/day	Oil Production/day, lb	lb BOD/ lb Oil	lb FAT/ lb Oil
Apr.	12,000	893	2,040	603,000	.0034	.00150
May	20,100	448	3,417	726,000	.0047	.00062
Jun.	15,900	587	2,703	803,000	.0034	.00073
Jul.	17,800	599	3,026	852,000	.0035	.00070
Aug.	20,800	1,066	3,536	829,000	.0043	.00128
Sep.	15,100	722	2,567	660,000	.0039	.00109
Total system in operation						
Jan. 1973	10,800	241	1,836	742,000	.0025	.00032
Feb.	6,800	139	1,156	1,021,000	.0011	.00014
Mar.	11,100	472	1,887	987,000	.0019	.00048
Apr.	22,100	517	3,757	1,047,000	.0036	.00049
May	9,900	568	1,683	861,000	.0019	.00066
Jun.	5,600	183	952	980,000	.0010	.00019
Jul.	6,800	430	1,156	835,000	.0014	.00052
Aug.	7,200	228	1,224	729,000	.0017	.00031
Sep.	5,500	424	935	733,000	.0013	.00058
Oct.	10,000	559	1,700	942,000	.0018	.00059
Nov.	9,600	496	1,632	900,000	.0018	.00055
Dec.	16,800	1,217	2,856	1,048,000	.0027	.00116

The overflow from the skimmer gravity flows to a sump where it is pumped to the clarifier. The clarifier is a 183,500 gal Rex Wastewater Clarifier (Figure C-1 of Appendix C). The clarifier is 50 ft in diameter with a surface area of 1950 sq ft. This provides an overflow rate of 75 gal per sq ft per day based on a flow of 150,000 gal per day. A 60 day average of clarifier influent versus clarifier effluent COD's resulted in an average reduction of 45% through the clarifier. Samples were based on 24 hour composites but were not flow proportioned. This data is presented in Table 16.

TABLE 16. CLARIFIER COD REDUCTION

Date	Influent COD (mg/l)	Effluent COD (mg/l)
11/08/71	1369	1316+
11/09/71	790	790
11/10/71	3579	1555
11/11/71	1790	1420
11/12/71	2900	1050
11/15/71	1970	579
11/16/71	3080	1100
11/17/71	2100	526
11/18/71	1840	684
11/19/71	2250	420
11/22/71	1840	920
11/23/71	2260	893
11/24/71	9731	2314
11/26/71	3550	1210
11/29/71	1210	1210
11/30/71	5030	2680‡
12/01/71	10000+	5360
12/02/71	4460	2310
12/03/71	3760	1900
12/06/71	2780	1700
12/07/71	2160	1440
12/08/71	8760	4950§
12/09/71	6000	1560
12/13/71	2580	2580
12/14/71	1540	2830
12/15/71	4740	2260
12/16/71	1800	1800
12/17/71	5665	3141#
12/20/71	1950	1900
12/21/71	825	2000
12/22/71	3500	1250
12/27/71	2407	1700
12/28/71	2064	1746
12/29/71	3326	1267
12/30/71	8750	3168#
1/03/72	1080	585
1/04/72	2455	1820
1/05/72	10000+	2300
1/06/72	2170	1171
1/10/72	2275	1455
1/12/72	3375	2250
1/13/72	1725	1725
1/14/72	3560	3000

TABLE 16. CLARIFIER COD REDUCTION (Continued)

Date	Influent COD (mg/l)	Effluent COD (mg/l)
1/18/72	1595	1740
1/19/72	2465	2247
1/20/72	1885	725
1/21/72	1667	943
1/24/72	1392	956#
1/26/72	2375	1241
1/31/72	1692	1692
2/01/72	1690	1400
2/02/72	2000	693
2/03/72	1181	1155
2/07/72	970	908
2/08/72	1196	700
2/09/72	1847	960
2/10/72	2000	763
2/11/72	1456	640
2/14/72	2408	2254
MEAN	2997	1642

*Reduction in COD is 45%.
+Acid liquor to lagoon.
‡Overflow soap-stock tank.
§Acid liquor to clarifier-black
#Corn oil.

Clarifier influent and effluent was monitored for 20 consecutive days from March 24 to April 14, 1972, and analyzed for fat, COD, pH, and temperature. This data is presented in Table 17 and Figures 15, 16, 17, and 18. Samples were taken on a 24 hour composite, but were not flow proportioned. A reduction in fat of 59% and a reduction in COD of 41% was noted.

The temperature of the effluent was stabilized at 34°C. The pH was slightly decreased throughout the period. The pH of the influent was high April 9 through April 11 due to a leaking seal on a caustic pump. The clarifier kept the pH below 9.5 throughout this period and returned to normal quickly after the seal was repaired.

High waste strength when the plant was on corn oil was primarily because corn oil was not degummed before refining. This was because no appreciable market for corn lecithin existed. Water soluble phosphatides are separated with the soapstock and some come out in the wash-water. Their gums are not readily precipitated by calcium chloride and a high wasteload results.

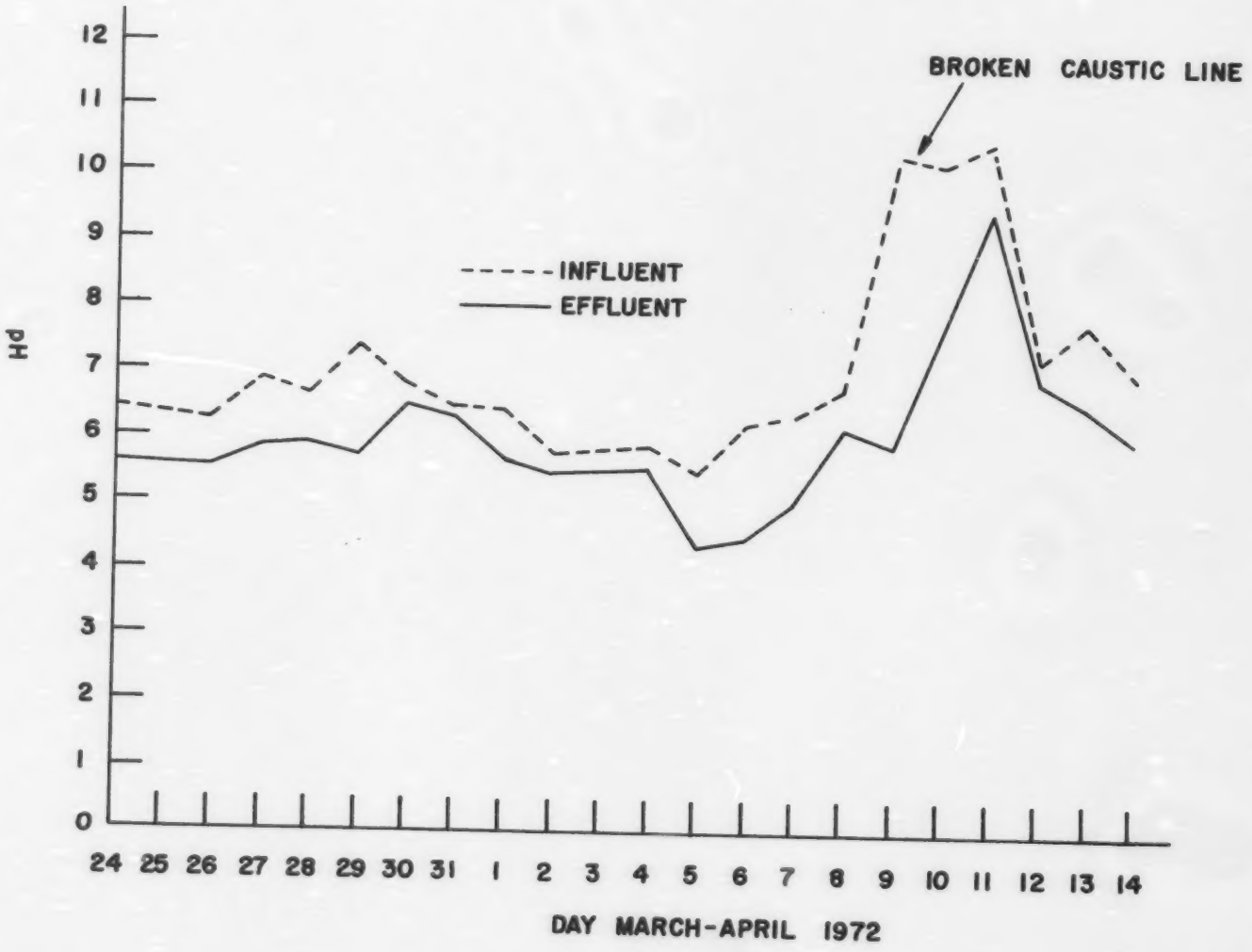


Figure 15. Clarifier pH vs day ADM Decatur.

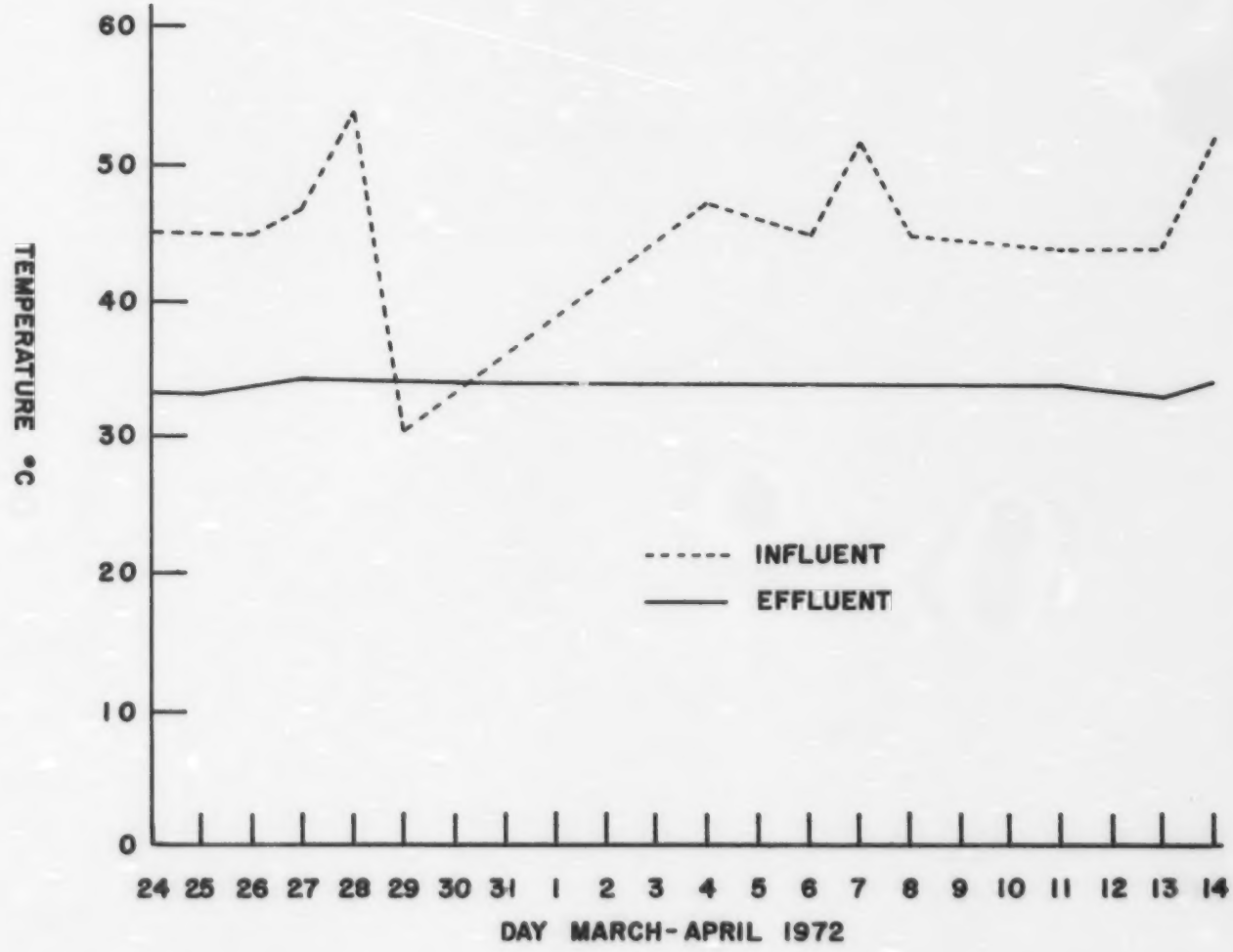


Figure 16. Temperature vs day ADM clarifier, Decatur, Illinois.

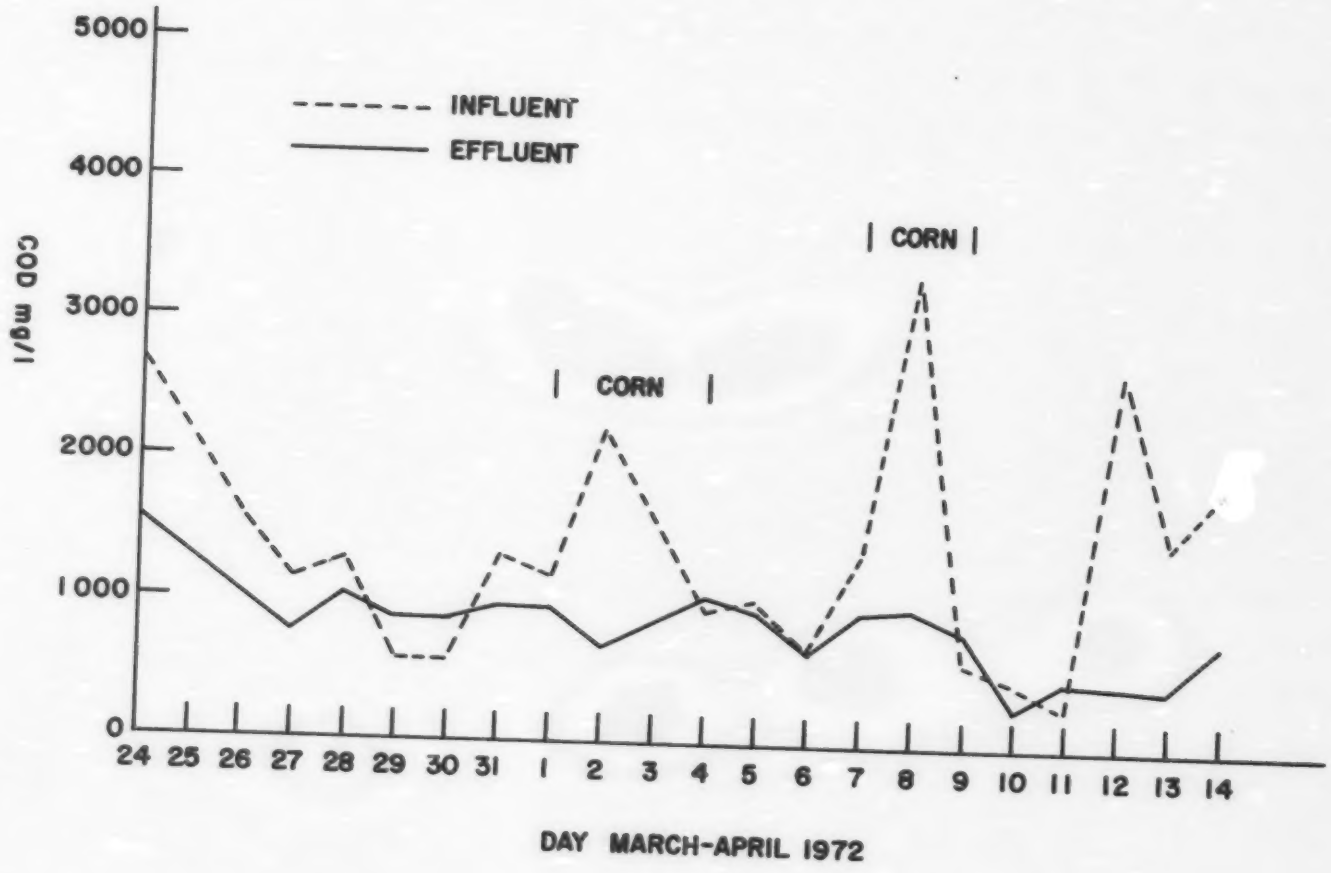


Figure 17. Clarifier COD vs day ADM Decatur.

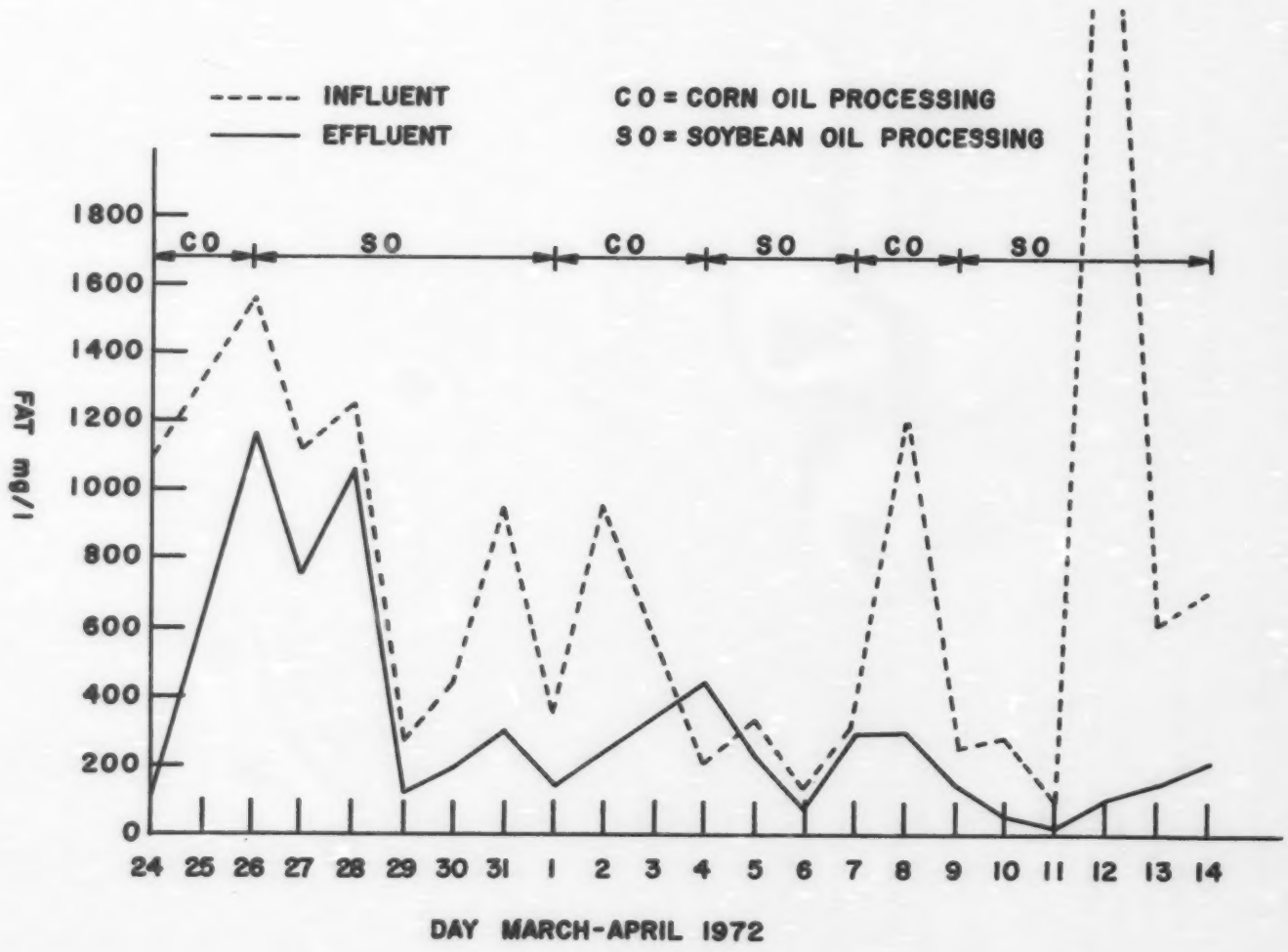


Figure 18. Fat vs day Decatur ADM clarifier.

Gums in the soapstock are not converted to fatty acids and remain in the acid water phase. This was and has remained a problem. However, since 1972 a small market for corn lecithin has been cultivated by sales, which has partially resolved the problem.

The COD of the acid liquor is highly variable depending on the nature of the soaps and the amount of floor washings in a particular batch. Therefore, the lagoon influent COD's give only a range of values that can be expected at a given time. The volume of acid liquor is approximately 25,000 gal per day produced in three or four equal batches. The steady increase in strength of the effluent indicates a need to clean the lagoon periodically, every two or three months. (Table 18)

Economic Analysis of Decatur West Refinery Waste Treatment System

From the process evaluation, it will be assumed fat losses were reduced .0036 lb per pound processed by the calcium chloride and clarification system. This is recovered as acid oil, the price of which is highly variable. This is an average of 3089 lb per day based on a daily production of 858,000 lb of oil. Table 19 is the total installation and operation cost of the calcium chloride treatment system and the clarifier. Tables 20 and 21 are a summary of waste treatment costs on a per lb BOD_5, per lb fat removed, per gal treated, and treatment cost per kg oil processed. The oil recovered must be processed by acidulation at a cost of 2¢ per lb.

The net cost is the treatment cost plus the cost of acidulation less the value of the recovered oil. This net cost ranges from .032¢ per kg oil processed to a gain of .063¢ per kg oil processed.

TABLE 17. DECATUR CLARIFIER OPERATION*

Date	pH	Fat (mg/l)	COD (mg/l)	Temp. (°C)	pH	Fat (mg/l)	COD (mg/l)	Temp. (°C)
3/25/72	6.4	1062	2737	45	5.6	118	1532	33
3/26/72	6.3	523	1560	45	5.5	302	1110	33
3/27/72	6.9	206	1110	46	5.8	347	742	34
3/28/72	6.6	430	1233	54	5.9	393	1053	34
3/29/72	7.4	128	544	30	5.9	267	816	33
3/30/72	6.8	203	560	--	6.5	427	806	--
3/31/72	6.5	935	1333	--	6.2	288	919	--
4/01/72	6.4	343	1161	--	5.8	241	969	--
4/02/72	5.8	917	2205	--	5.4	162	694	--
4/04/72	5.9	204	959	47	5.5	464	1030	34
4/05/72	5.4	327	1030	45	4.3	225	964	34
4/06/72	6.2	130	659	52	4.4	65	659	34
4/07/72	6.3	290	1364	45	5.0	280	968	34

TABLE 17. DECATUR CLARIFIER OPERATION* (Continued)

Date	pH	Fat (mg/l)	COD (mg/l)	Temp. (C°)	pH	Fat (mg/l)	COD (mg/l)	Temp. (C°)
4/08/72	6.7	1216	3416	--	6.1	270	960	--
4/09/72	10.3	244	627	--	5.8	133	808	--
4/10/72	10.1	253	454	--	7.6	66	250	--
4/11/72	10.4	47	247	44	9.4	18	418	34
4/12/72	6.9	2136	2757	44	6.8	87	467	33
4/13/72	7.7	613	1421	53	6.4	118	433	34
4/14/72	6.9	682	2375	--	5.9	191	773	--
Average		544	1388			223	818	

*Reduction is 59% for fat and 41% for COD.

TABLE 18. LAGOON OPERATION COD (mg/l)*

Date	Influent	Effluent
1/05/72	14,600	3,580
1/15/72	8,650	5,600
2/07/72	11,475	6,235
2/22/72	7,618	7,194
2/28/72	19,260	9,250
3/06/72	14,250	10,000
Average	12,642	6,976

*COD removal is 45%.

TABLE 19. INSTALLATION AND OPERATION COSTS FOR WEST REFINERY WASTE TREATMENT SYSTEM

Item	Cost per year
Calcium Chloride (Costs for 1969):	
Depreciation @ 10% per year based on total capitalized cost of $25,000	$ 2,500
Calcium Chloride @ 7¢ per lb dosage of 0.25%	21,308
Maintenance	1,000
Labor 4 hours per day	7,500
	$ 32,308
Clarifier (Costs for 1971):	
Depreciation @ 5.5% per year based on total capitalized cost of $96,621	$ 5,367
Utilities	5,000
Interest	9,662
Insurance and Taxes	1,932
Maintenance	
Mechanical 5%	5,000
Structures	1,000
Labor 1 man	15,000
	$ 42,961
Total Treatment Cost	$ 75,269

TABLE 20. SUMMARY OF TREATMENT COSTS

Item	$CaCl_2$ Treatment	Clarifier	Total
Cost per day	$ 88	$118	$206
BOD removal (lb per day)	8236	1716	9952
Cost ¢ per lb BOD removed	1.06	6.87	2.07
Fat removal (lb per day)	2660	420	3080
Cost ¢ per lb fat removed	3.3	28.1	6.7
Cost ¢ per gal (based on 150,000 gal per day)	.059	.077	.136
Cost ¢ per kg oil produced	.019	.026	.045

TABLE 21. NET COSTS (COST MINUS REVENUES*)

Acid Oil Price	Cost per 1000 liters	Cost per 1000 gal	Cost per kg Oil Processed
4¢ per lb	$.251	$0.95	.032¢
18¢ per lb	-$.510	-$1.93	-.063¢

Revenue: 4¢ per lb Acid Oil Revenue = (.04-.02) (3080) = $61.76 per day;
18¢ per lb Acid Oil Revenue = (.18-.02) (3080) = $494.08 per day.

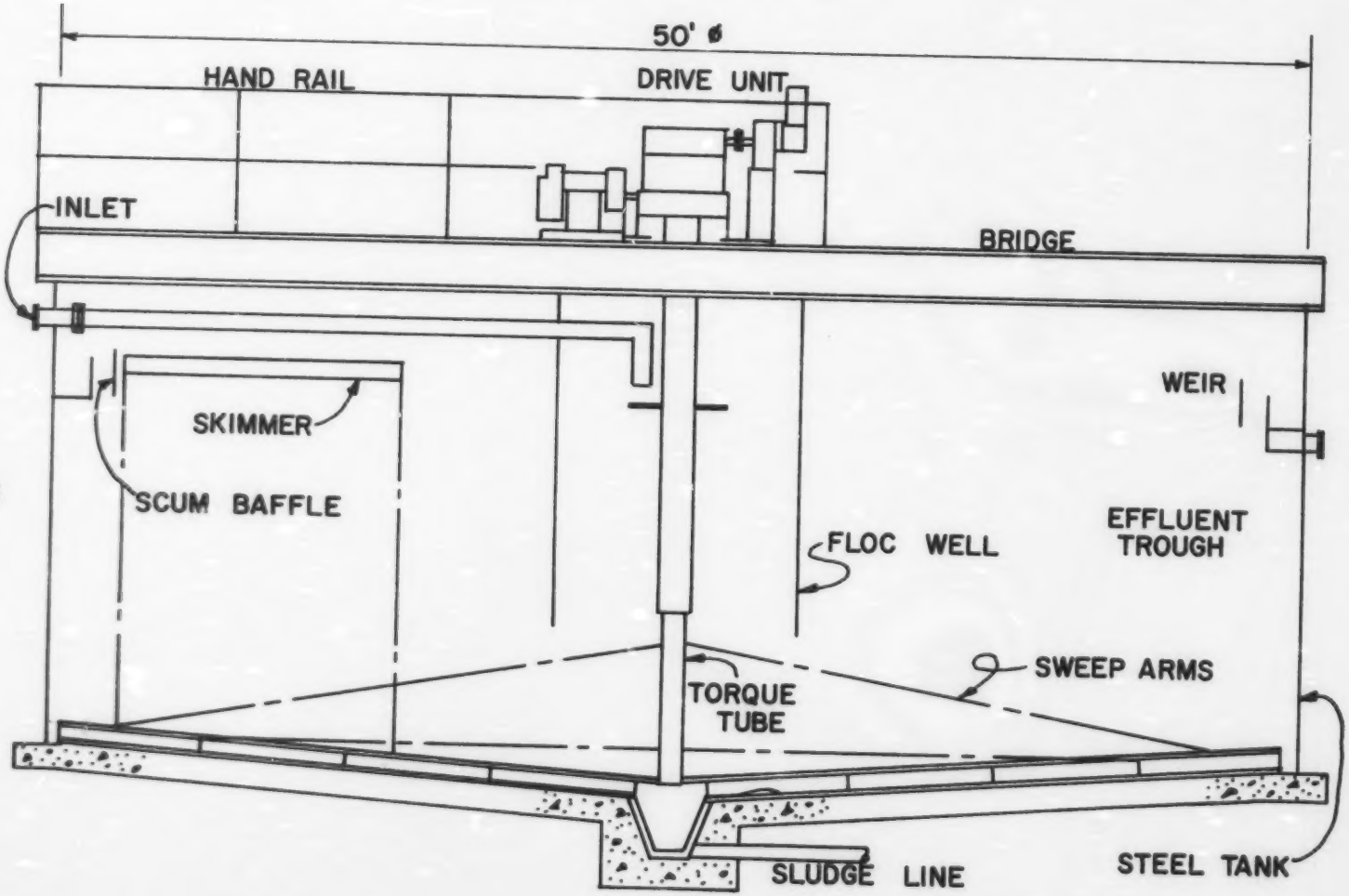


Figure A-1. Rex wastewater clarifier (186,500 gallons).

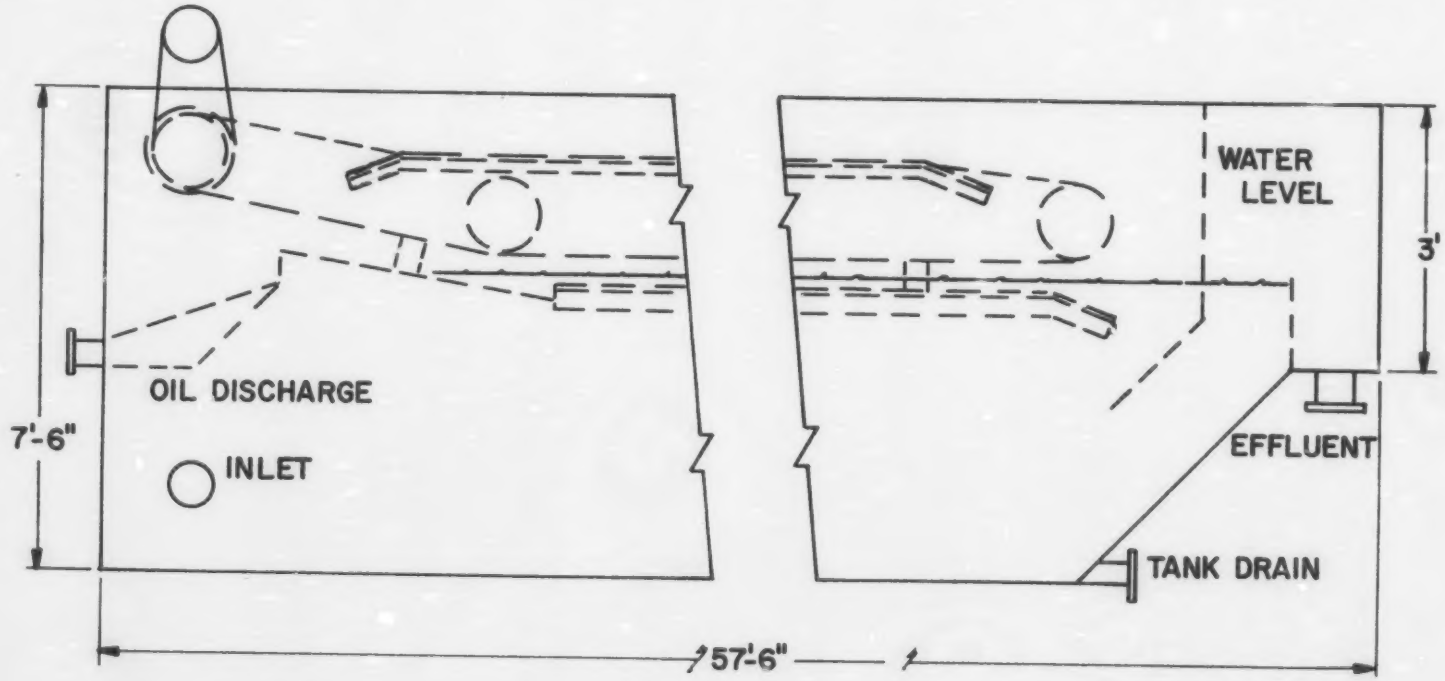


Figure A-2. Walker skimmer.

APPENDIX B. ANALYTICAL PROCEDURES

Fats, Oils, and Greases - Analytical Procedure Used During R.F.W. Survey

1. The samples were thoroughly shaken (and heated, if necessary) and were acidified with 5 ml of concentrated H_2SO_4 and heated on a steam bath for 15 to 30 minutes.

2. The samples were cooled and 50 ml of hexane added to the sample bottle (100 mg of hexane was added if an overabundance of grease was present).

3. The sample bottle was shaken manually for 30 seconds at about 240 shakes per minute rate.

4. The entire contents of the bottle were poured into a one-liter separatory funnel and allowed to separate. The water layer was decanted into a one-liter graduated cylinder and the volume recorded. The hexane was then allowed to filter through a filter-cel precoated, whatman No. 1 covered, buchner funnel. The precoat consisted of about 30 ml of a 10 gm/l slurry of filter-cel.

5. The sample bottle, transfer funnel, and separatory funnel were rinsed with about 10 - 15 ml of hexane and this was added to the 50 ml and also filtered.

6. The filtered hexane was collected in test tubes in the vacuum flasks and transferred to 30-ml capacity, pre-tared aluminum weighing dishes and evaporated on a steam hot plate. Any water-hexane emulsion was also filtered and evaporated.

7. The evaporated dishes were placed in a 103°C oven for at least one hour, transferred to a desicator and re-weighed.

8. Fats, oils, and greases, mg/l =

$$\frac{\text{Final Weight in mg} - \text{Initial Weight of Dish in mg}}{\text{ml sample}} \times 1000$$

A-D-M COD Test Procedure

1. Prepare sample of aliquot and place in 250 ml reflux flask. (Size of sample depends on strength of aliquot - 10 ml if COD is 1000 below or proportionately less if COD is higher.)

2. Add 10 ml potassium dichromate (0.125 n), 15 ml conc. sulfuric acid and pumice to each flask and reflux for 15 minutes.

3. Set control and titrate with ferrous ammonium sulfate (0.067 n) to determine normality $\frac{.125}{\text{ml used}}$ (10 ml potassium dichromate, 15 ml conc. sulfuric acid, cool to 60°C, add 3 drops ferroin[1], 50 ml distilled water and titrate).

4. After 15 minutes cool flask to below 60°C and titrate with ferrous ammonium sulfate (0.067 n) recording ml used.

5. Calculate COD = $\frac{\text{A-B x normality} \times 8000}{\text{ml of sample}}$

   A = ml of titrant for control
   B = ml of titrant for sample

   Normality = $\frac{1.125}{\text{ml of control}}$

[1]Ferroin Indicator = 1.485 grams 1.10 Phenanthroline and 0.695 grams Ferrous Sulfate per 100 ml distilled water.

APPENDIX C. WASTE TREATMENT FACILITIES AT ADM, LINCOLN, NEBRASKA

The calcium chloride treatment is essentially the same as that in Decatur and will not be discussed here.

All refinery effluent is pumped to a 30,000 gal split box where it is skimmed and overflows to a series of sumps where it is mixed with blowdown from the barometric condenser cooling tower and pumped to the skimmer. The skimmer effluent is pumped to the clarifier. The water from the clarifier flows through the sampling station to the sanitary sewer. (Figure C-1)

The water from acidulation is also pumped to the split box. The clarifier water is always dark in color due to the acid liquor; however, the clarifier does an effective job of BOD_5 removal. Acidulation, a major contributor to the sewer load, was shut down in May 1971 and started again in September when the clarifier was put into operation. A drop in the sewer load was noted when acidulation was shut down and no increase was noted when it was started again with the clarifier in operation. Refer to Figures C-2, C-3, C-4, and Table C-1. Therefore, a before and after comparison was made for the period after the clarifier was started and before acidulation was shut down.

TABLE C-1. ANALYSIS OF DISCHARGE TO MUNICIPAL SEWER

Month	COD (lb/day)	Suspended Solids (mg/l)	Fat (mg/l)
Jan. 1971	3191	756	310
Feb.	4128	982	571
Mar.	4467	780	508
Apr.	4116	735	484
May	1589	272	233
Jun.	1182	256	206
Jul.	1590	248	229
Aug.	1907	309	246
Sep.	1497	209	213
Oct.	1589	225	229
Nov.	1510	183	181
Dec.	1472	155	160
Jan. 1972	1765	145	5150
Feb.	1118	199	99
Mar.	662	97	73

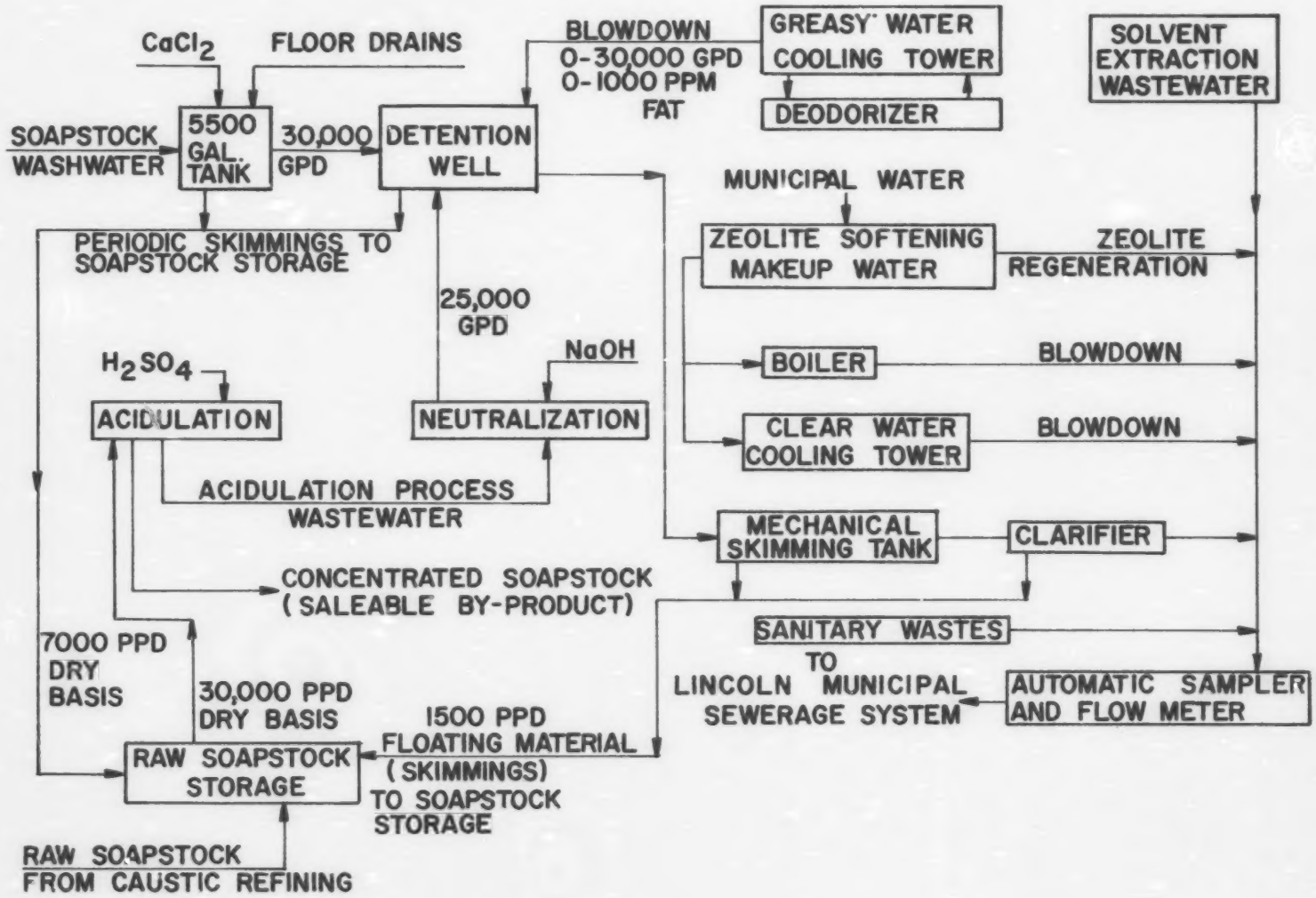


Figure C-1. Lincoln wastewater treatment facility.

These data are presented in Figures C-2, C-3, and C-4. A comparison of parameters for January - April, 1971 with October 1971 - March 1972 gives the following average reductions:

Parameter	% Reduction
Fat	66.3
SS	78.7
COD	65.6

The higher reduction in suspended solids was expected, since this type of material is treated especially well by the clarifier.

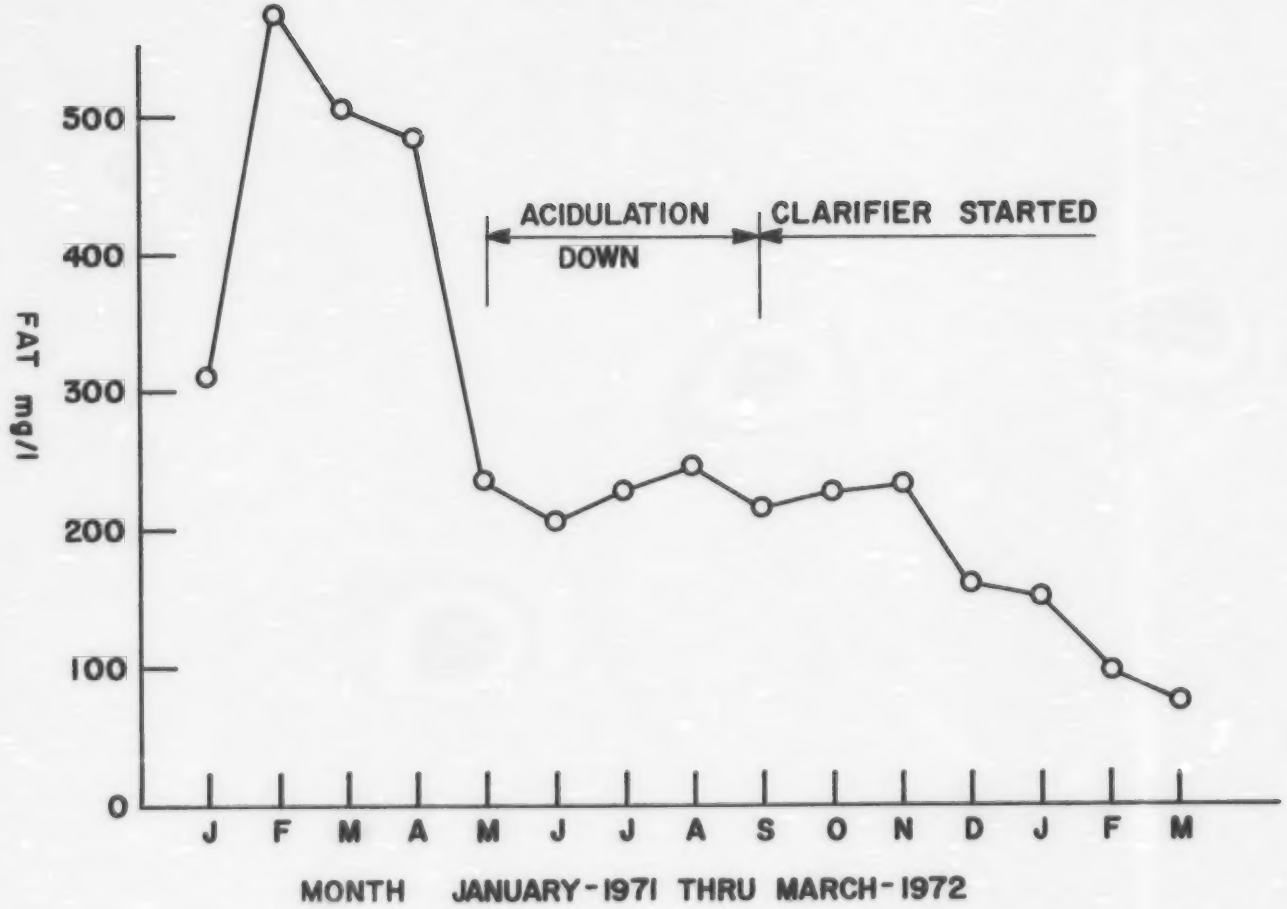


Figure C-2. ADM Lincoln, Nebraska average mg/l fat vs month January 1971-March 1972.

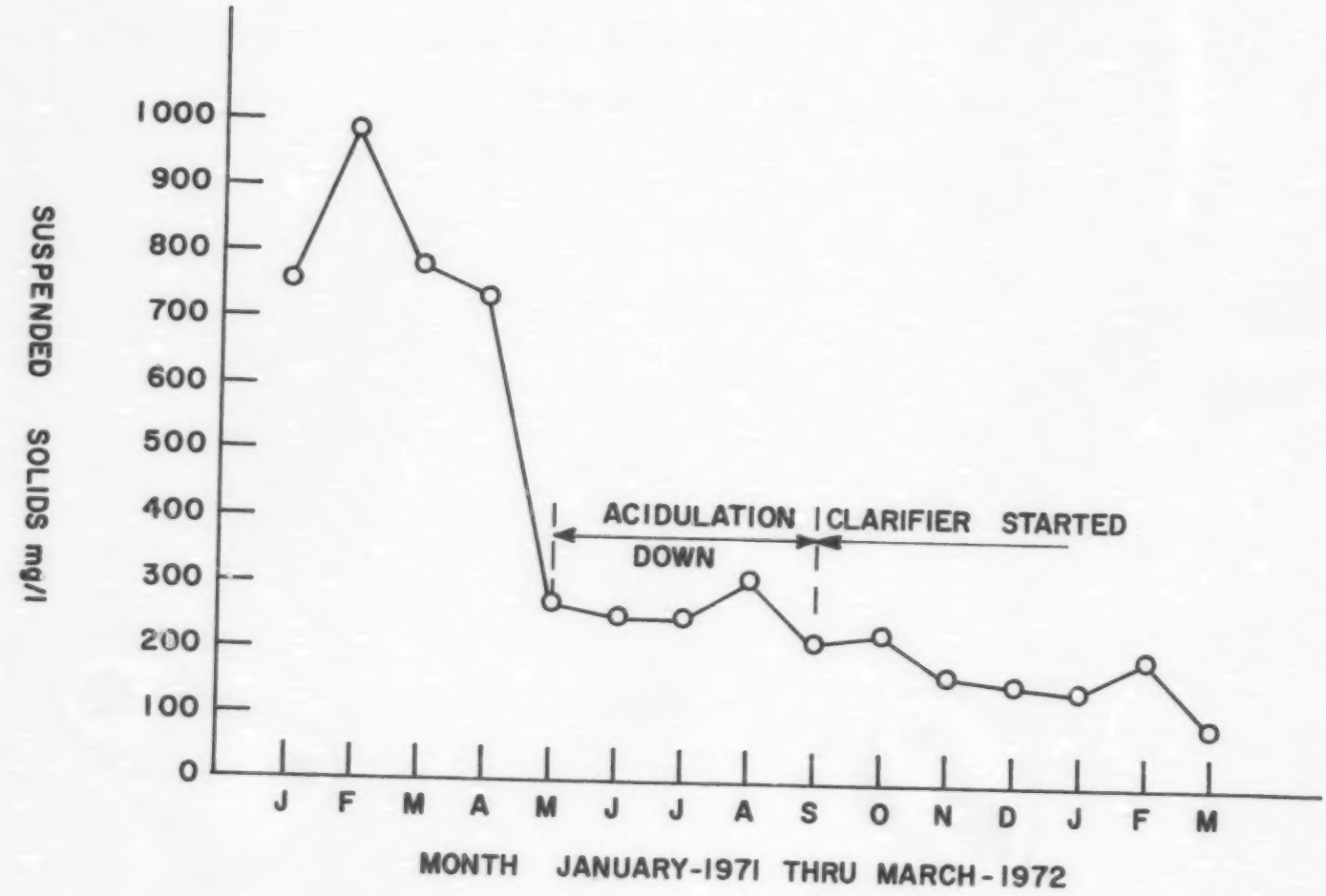


Figure C-3. ADM Lincoln, Nebraska suspended solids vs month January 1971-March 1972.

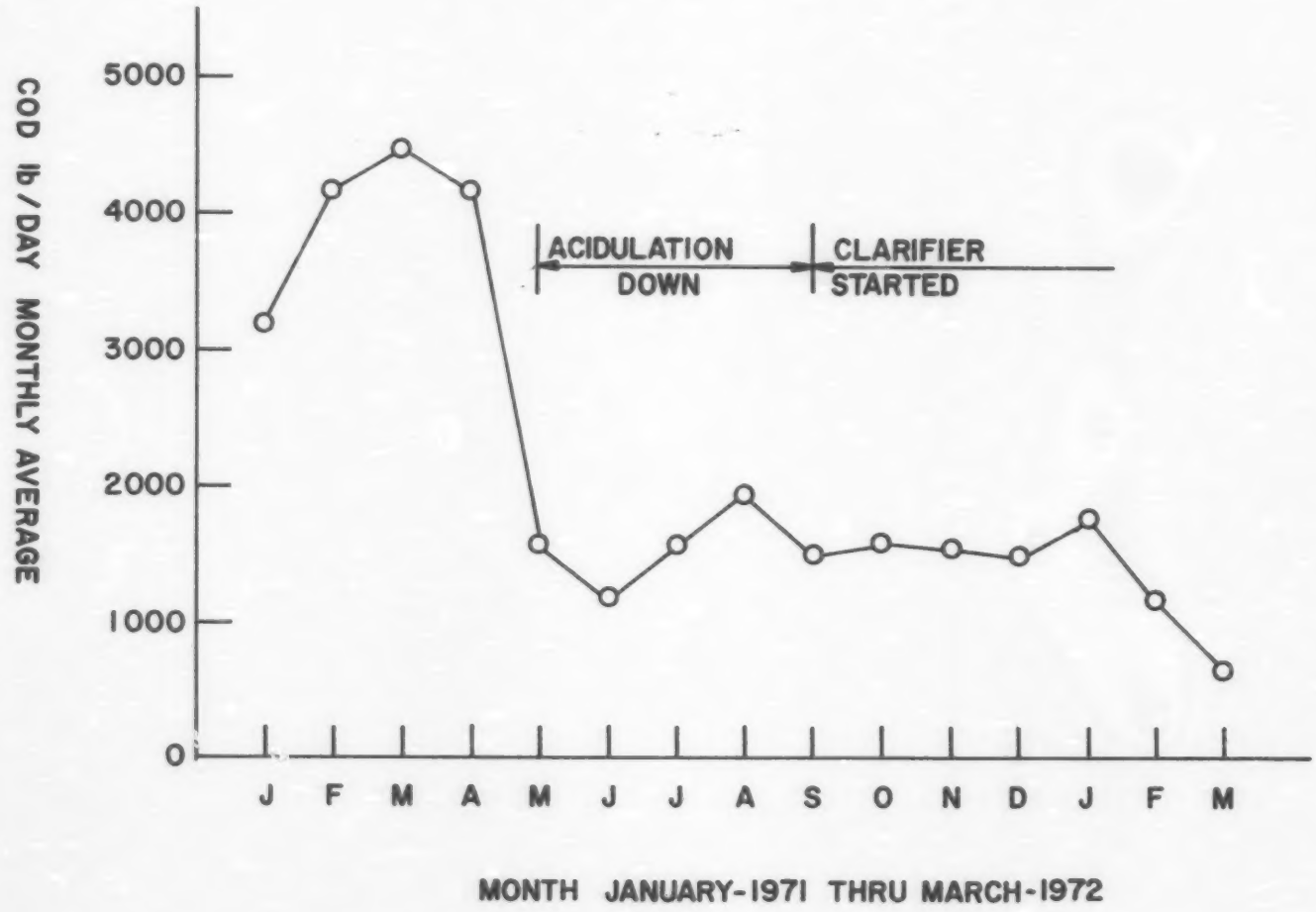


Figure C-4. ADM Lincoln, Nebraska average lb OOD/day vs month January 1971-March 1972.

SECTION X

BIBLIOGRAPHY

Bailey, A. E. Industrial Oil and Fat Products, New York, Interscience Publishers, Inc. 1945.

Standard Methods for the Examination of Water and Wastewater, 12th Edition. New York, American Public Health Association. 1965.

Weston, R. F. "Conceptual Design Report, Upgrading of West Plant Wastewater Treatment Facilities. West Chester, Pennsylvania. January 1970.